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A METHODOLOGY FOR DETERMINING THE EFFECTS OF FUELS AND ADDITIVES ON ATMOSPHERIC VISIBILITY

W. C. Kocmond, et al

Calspan Corporation

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A methodology for determining the effects of fuels and additives on atmospheric visibility has been developed using the smog chamber approach. The methodology involves measuring visibility in a 590 m^3 smog chamber after first introducing auto exhaust at a 300:1 detection ratio adding 0.05 ppm SO_2 and irradiating the sample for 23 hours. Three 5.7 liter 1972 Chevrolets and one 1973 catalyst-equipped 6.55 liter Ford Galaxie were used in the study. The effects on test results of exhaust dilution ratio, relative humidity, added SO_2, primary particulates, evaporative emissions and irradiation time are discussed. The tests show that using commercial grade indolene fuel, the effects on visibility of the additives F-310 and CI-2 are small compared to the effects brought about by variations in engine performance. The presence of primary particulates play an important role in the initial and final visibility noted in the smog chamber. Irradiations of particle-free HC + NO + SO_2 mixtures comparable to those found in auto exhaust did not produce equivalent visibility losses. The final visibilities noted in the smog chamber were found to be closely correlated with the initial HC/NO ratio. The correlation for the commercial grade indolene is so good that final visibilities can be predicted from the initial measurement of HC and NO in the chamber. Data generated using EPA reference fuel show a similar correlation of visibility with HC/NO ratio, but the data lie on a different straight line (due to lower sulfur content of fuel). For the fuels and additives tested at a given HC/NO ratio, the sulfur content of the fuel appeared to have the most important effect on visibility.

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by

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June 1975

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The tests show that using commercial grade indolene fuel, the effects on visibility of the additives F-310 and CI-2 are small compared to the effects brought about by variations in engine performance. The presence of primary particulates plays an important role in the initial and final visibilities noted in the smog chamber. Irradiations of particle-free HC+NO+SO_2 mixtures comparable to those found in auto exhaust did not produce equivalent visibility losses.

The final visibilities noted in the smog chamber were found to be closely correlated with the initial HC/NO ratio. The correlation for the commercial grade indolene is so good that final visibilities can be predicted from the initial measurement of HC and NO in the chamber. Data generated using EPA reference fuel show a similar correlation of visibility with HC/NO ratio, but the data lie on a different straight line (due to lower sulfur content of fuel). For the fuels and additives tested at a given HC/NO ratio, the sulfur content of the fuel appeared to have the most important effect on visibility.

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Section 1

INTRODUCTION

One of the provisions of the 1970 amendment to the Clean Air Act stipulates that the Administrator of the Environmental Protection Agency (EPA) may require a fuel or fuel additive manufacturer to conduct specific tests in accordance with accepted test methods and procedures to determine the effect of such emissions on the public welfare or on the emission control performance of a vehicle. The contribution of these emissions to reduced visibility in the atmosphere is related to this problem and therefore must also be considered. In order to anticipate possible regulatory measures, a methodology is required for assessing the effects of fuels and/or fuel additive combustion products on atmospheric visibility. It has been the objective of this investigation to develop such a methodology.

The effect of automotive exhaust emissions on atmospheric visibility is greatly magnified by processes of photochemical aerosol formation. The methodology must therefore be based on a realistic simulation of normal atmospheric irradiation conditions. While the objective is to assess variabilities in the ultimate visibility effects corresponding to differences in the types of fuels and additives, evaluation tests must be performed on exhaust products of the respective fuels and additives. There is, therefore, a need to standardize the vehicle engine operating procedures to minimize inadvertent alterations in vehicle emission characteristics. These factors have been taken into consideration.

As part of the methodology development, three 1972 Chevrolets with 350 CID engines were operated on low-lead and non-leaded indolene fuel of the same base stock while mileage accumulation, emission analyses, and smog chamber tests were performed. Part of the testing included chamber experiments to determine the effects of the additives F-310 and CI-2 on exhaust emissions and atmospheric visibility. After the 16,100 km (10,000 mile) accumulation point was reached, the engines of the test vehicles were cleaned, and additional experi-

ments were performed on two of the cars using EPA reference fuel of low sulfur content. A replacement third car, a 1973 Ford Galaxie 500 equipped with a catalytic converter and operating on both the low sulfur and a 0.1% sulfurated fuel, was also evaluated during the final phases of the study.

Within this report, descriptions of the experimental facilities used in the investigation are provided and results of the methodology development, interpretations of the data, and recommendations for implementation of the methodology are given.

Section 2

EXPERIMENTAL FACILITIES

2.1 The Calspan Smog Chamber

The main facility used in developing the methodology was the 590 m^3 (20,800 ft^3) Calspan smog chamber. The chamber, shown in Figures 1 and 2, is constructed of 1.3 cm (0.5 in.) thick steel walls and is 9.1 meters (30 feet) in diameter and 9.1 meters (30 feet) high. The inner walls of the chamber are coated with a specially formulated fluoroepoxy, which is similar to teflon in surface characteristics.

Lighting within the chamber is provided by a combination of fluorescent daylight, blacklamp and sunlights installed inside 24 modules and arranged in 8 vertical channels attached to the wall of the chamber. Each module contains two 215-watt F96PG17/D daylight lamps, eight 85-watt P72T12HO blacklights, and two 40-watt FS40 sunlamps giving a total of 28.5 kw of power. The modules are covered with 0.64 cm (0.25 in.) annealed Pyrex panels which are used to isolate the lamps from the chamber atmosphere. The measured light intensity of the system was found to be $k_d[NO_2] \sim 0.23\ min^{-1}$ or approximately 50% of noonday sun intensity. More recent modifications to the chamber lighting system have resulted in a measured $k_d[NO_2] \sim 0.35\ min^{-1}$; however, in order to maintain continuity throughout this investigation, all experiments were performed at the former light level.

Air purification is achieved by recirculating the chamber air through a series of absolute-plus-charcoal filters, Figure 3. Particle concentrations of less than 100 cm^{-3} and levels of NO_x <0.01 ppm, O_3 <0.001 ppm, and SO_2 <0.001 ppm are routinely obtained after eight hours of filtration.

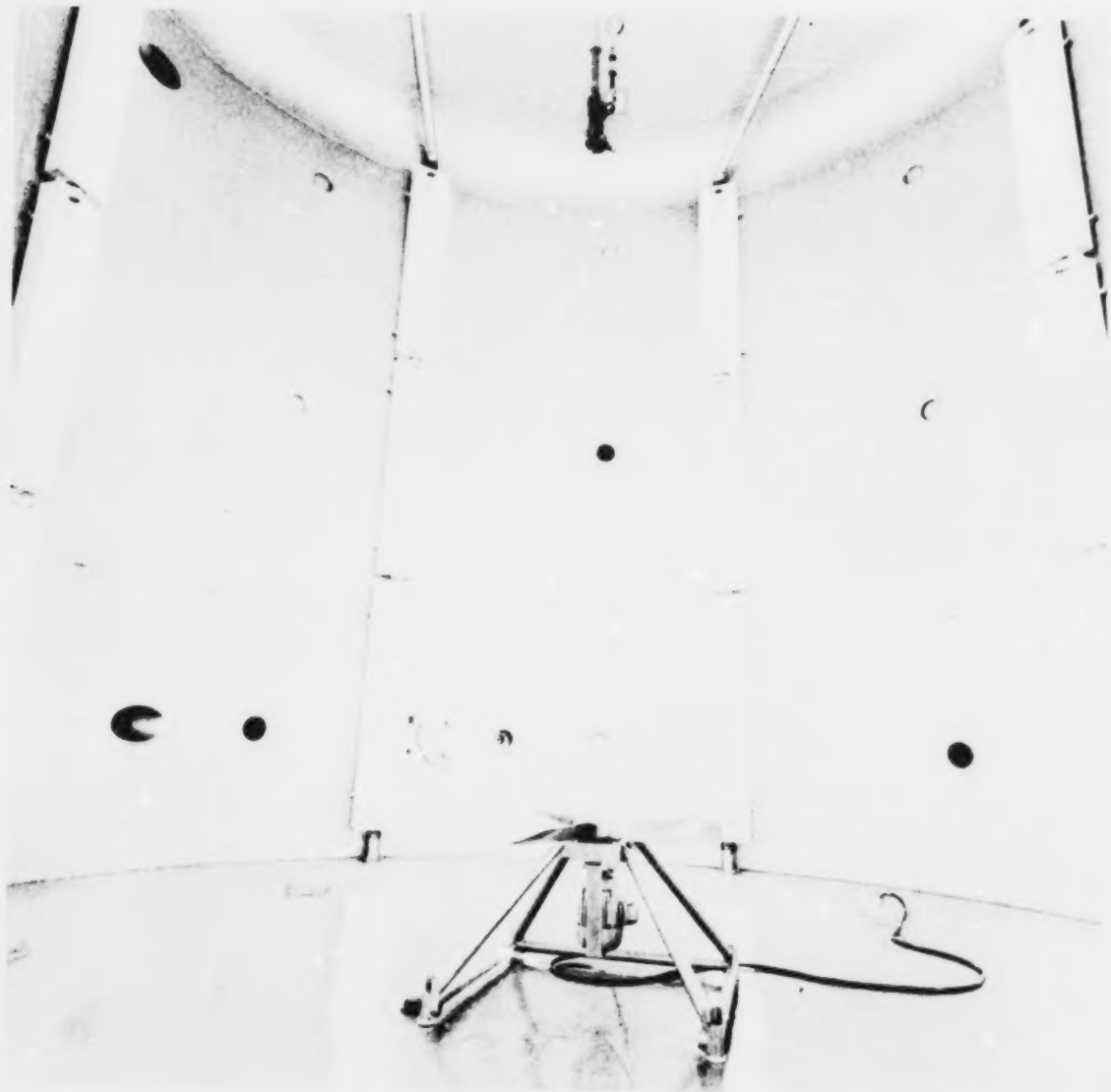

Figure 1 INSIDE VIEW OF CALSPAN'S 590m^3 PHOTOCHEMICAL AEROSOL CHAMBER

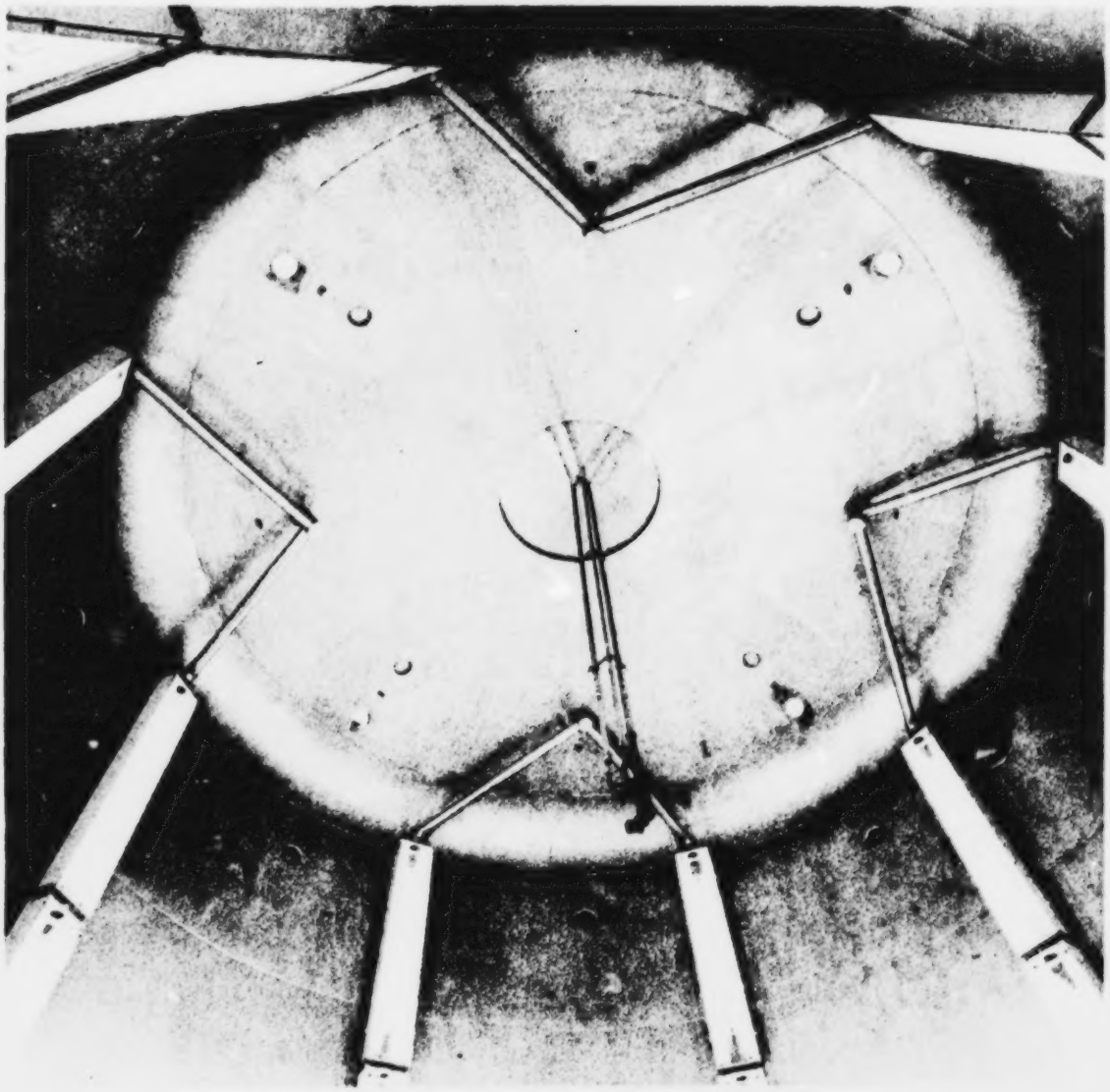

Figure 2 INSIDE VIEW OF TOP AREA OF CALSPAN'S 590m^3 PHOTOCHEMICAL AEROSOL CHAMBER

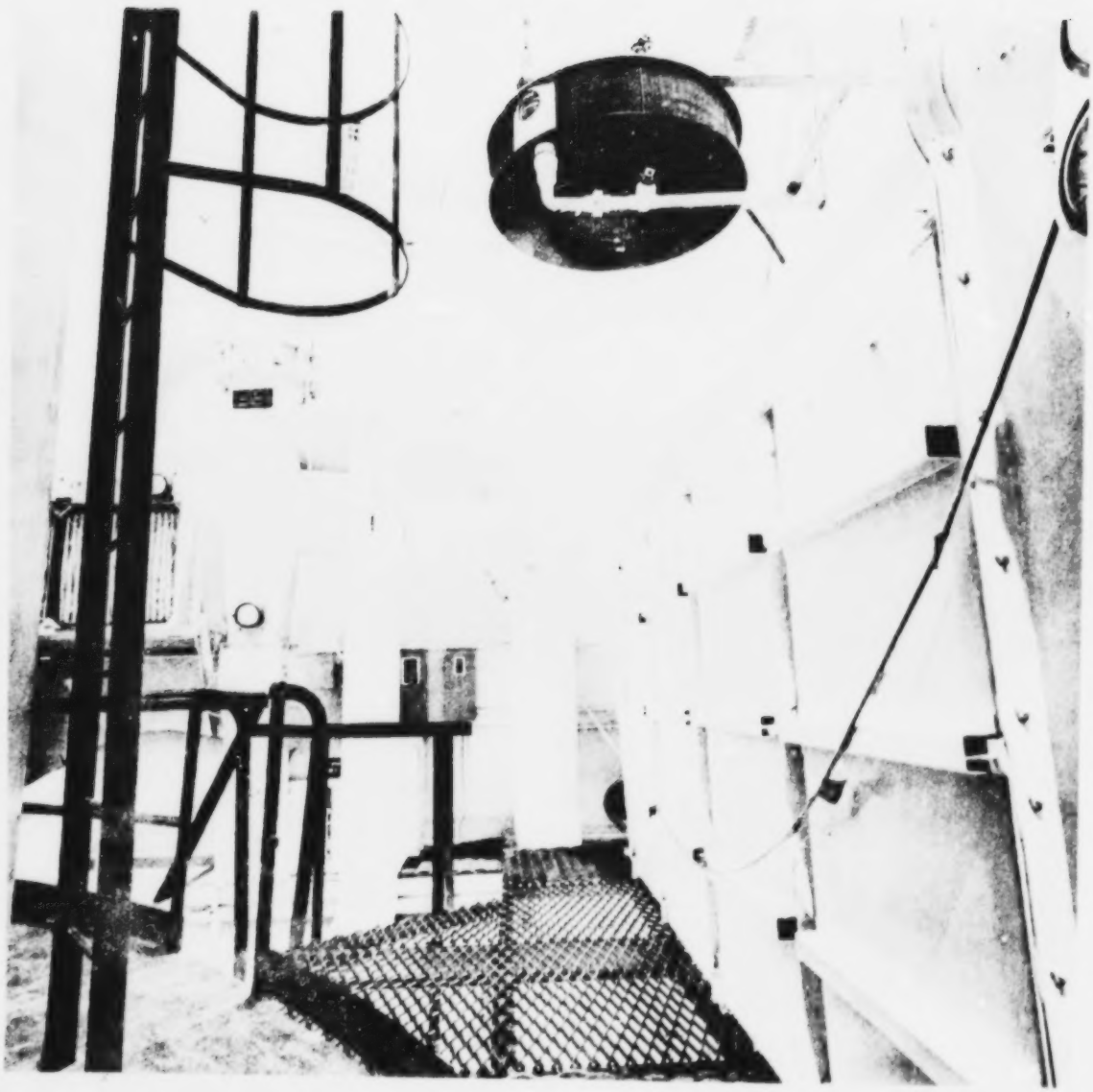

Figure 3 VIEW OF AIR CIRCULATION SYSTEM CONTAINING DUCTWORK AND CHARCOAL FILTERING BEDS

2.1.1 Instrumentation

Gas and particle analysis equipment that was used includes the following:

(1) Bendix Model 8002 Ozone Analyzer -- This instrument is based on the principle of photometric detection of chemiluminescence resulting from the reaction of ozone with ethylene. The minimum detectable sensitivity is 0.001 ppm.

(2) Bendix Model 8101-B Nitrogen Oxides Analyzer -- Detection is based on chemiluminescent reaction between nitric oxide and ozone. The detection limit for each of the nitrogen oxides is 0.005 ppm.

(3) Bendix Model 8300 Sulfur Analyzer -- Operation of this instrument is based on the photometric detection of sulfur atoms excited in a hydrogen-rich flame. A set of scrubbers is used for selective monitoring of sulfur dioxide and hydrogen sulfide. The minimum detectable sensitivity is 0.005 ppm.

(4) Bendix Model 8201 Reactive Hydrocarbon Analyzer -- Flame ionization detection provides analysis of methane (CH_4), total hydrocarbons (THC), and reactive hydrocarbons (THC-CH_4).

(5) Hewlett-Packard Model 5750 Gas Chromatograph -- The chromatograph is equipped with dual column and dual flame ionization detectors. Depending on the column in use, either total hydrocarbon or individual components can be analyzed. Detection limits of 0.01 ppm are achievable.

(6) Meteorology Research Inc. Model 1550 Integrating Nephelometer -- In operation, an air sample is drawn through a chamber where it is illuminated by light from a pulsed flash lamp. The scattered light is detected by a photomultiplier and compared with a reference voltage from another phototube. The nephelometer provides a measure of the scattering coefficient of the aerosol which, in turn, is related to meteorological visual range. Observations of visibility can be made in the range of ~0.5 km (~0.3 miles) to >160 km (>100 miles).

(6) Gardner Small Particle Detector -- Used to measure total particle concentration in the range of 10^2 to 10^6 cm^{-3}. Particle concentration is determined by nucleation of particles at high supersaturation, followed by observation of light attenuation within a small cloud chamber. Minimum detectable particle size is about 0.002 μm.

(7) Environment One Model 100 Condensation Nucleus Monitor -- This instrument operates on the same principal as the Gardner Small Particle Detector; however, automatic measurement and recording features are included. The minimum particle size detected is claimed to be 0.0025 μm. A number of problems were encountered during the operation of this instrument, and no data were acquired during several of the experiments. The instrument was not used for the Phase II methodology tests.

(8) Thermo Systems Inc. Electrical Aerosol Analyzer (EAA) -- Late in the program an EAA was obtained and used for size distribution analysis of the smog aerosol. Actual delivery of the instrument was delayed until March 1974 so that only limited use could be made of the instrument. Operation of the EAA is based on the fact that the mobility of particles decreases with increasing particle size for particles less than 1 μm. In operation, the aerosol is charged with negative ions generated by a corona discharge in the charger. The aerosol emerges from the charger and flows to the mobility analyzer for analysis. From the mobility spectrum obtained, the particle size distribution can be inferred. The range of particle size measurement is from 0.004 μm to ~0.4 μm.

In addition to these instruments, special provisions were made to transfer the Calspan vehicle emissions laboratory from Buffalo, N.Y. to our Ashford smog chamber site. The system, which includes a chassis dynamometer and sampling analysis equipment, is described in the following section.

2.2 Vehicle Emissions Research Laboratory (VERL)

One of the program requirements stipulates that all tests be performed in accordance with procedures set forth in the Federal Register, Vol. 37, No. 10. In order to do so, the emissions laboratory and dynamometer were transferred to a specially built garage adjacent to the smog chamber.

In operation, vehicles were driven over the LA-4 driving cycle on a chassis dynamometer while a given quantity of exhaust gas and ambient air was collected with a positive displacement gas sampler and transferred to Tedlar storage bags. (When smog chamber tests were being run, a fraction of the exhaust gases were diverted into the chamber before entering the CVS system.) The sampling system, shown in Figure 4, consists of exhaust tubing, a series of ambient air filters, a mixing chamber, heat exchanger, positive displacement pump, four-speed, seven h.p. motor, four Tedlar collection bags, final exhaust dumping hose, and necessary controls. To ensure a constant volumetric flow, the gas mixture was kept at constant temperature by passing through a heat exchanger. After storing a portion of the exhaust gas/ambient air mixture in inert bags, the contents of the bags were transferred to the gas analyzers for determinations of carbon monoxide, carbon dioxide, total hydrocarbons, and oxides of nitrogen.

The concentrations of HC, CO, CO_2, and NO_x were measured by four multirange analyzers. Two nondispersive infrared analyzers (NDIR) were used to measure CO and CO_2. Total HC were measured by a flame ionization detector, and oxides of nitrogen were measured by a chemiluminescent analyzer. A complete listing of the pertinent equipment used in the emissions laboratory on this program is shown in Table I.

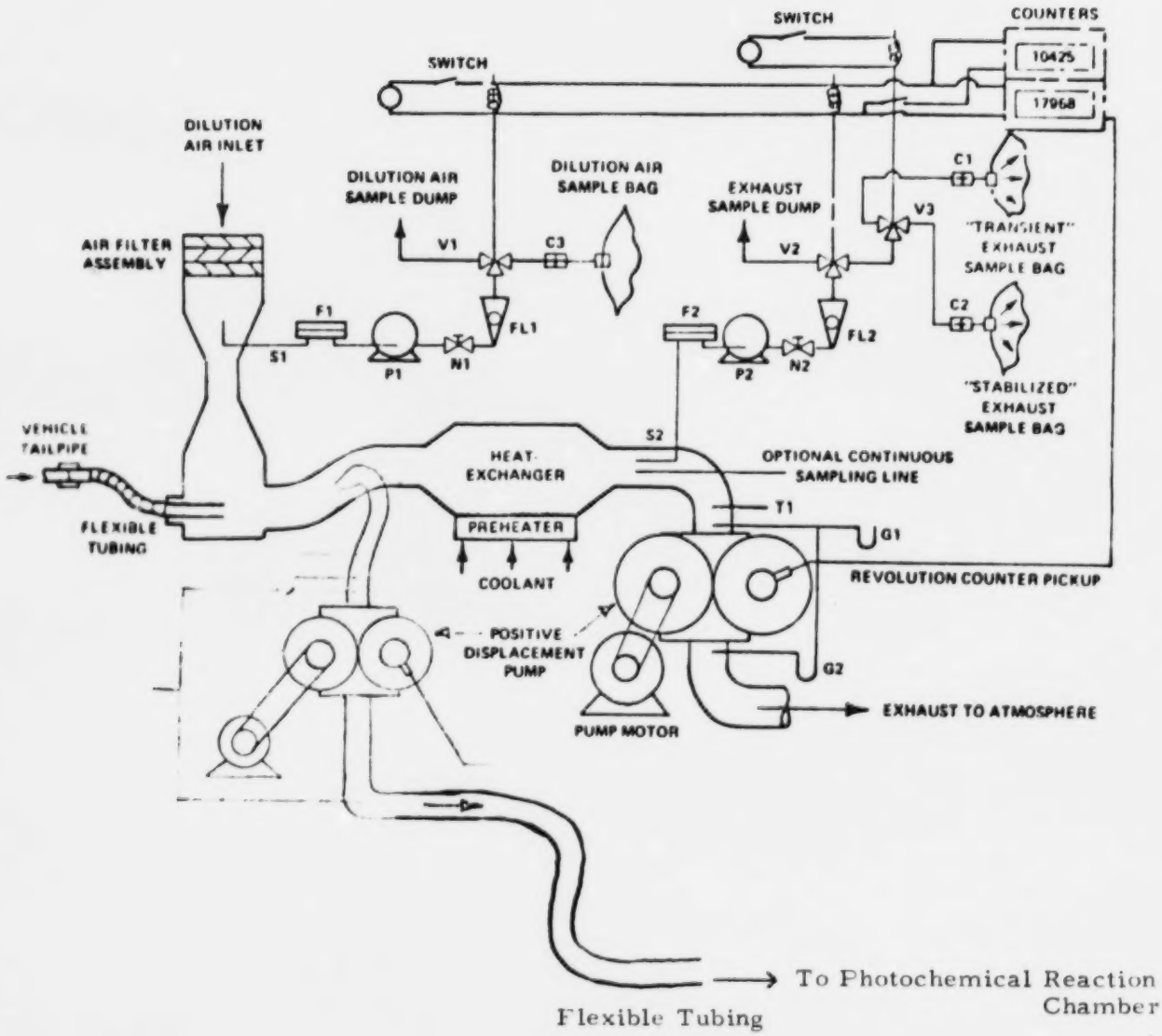

FIGURE 4. VEHICLE EXHAUST SAMPLING SYSTEM

Table I.

EMISSIONS LABORATORY SUPPORT INSTRUMENTATION

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UNIT	MODEL	DESCRIPTION
CHASSIS DYNAMOMETER	CLAYTON CT-50 (VIF)	SPLIT ROLLERS; ECHO ABSORPTION UNIT; STRAIN GAGE TORQUE BRIDGE; AIR-ACTUATED WHEEL LIFTS; MANUALLY CONTROLLED VARIABLE INERTIA FLYWHEELS (VIF); INERTIA WEIGHTS FROM 1500 TO 3000 lb IN 250-lb INCREMENTS AND FROM 3000 TO 5500 lb IN 500-lb INCREMENTS.
DRIVER'S AID	VARIAN G1000	SINGLE-PEN, FIXED-SPEED STRIP CHART RECORDER; CONTROLS MOUNTED ON FACE COVER.
ENGINE COOLING FAN	HARTZELL N24-DU	FIXED-SPEED, 52-in. cfm, PORTABLE CHASSIS.
ENGINE ANALYZER	SUN EET-1160	22-in. SCOPE, VOLT LEAK UNIT; TACH DWELL UNIT; COMB-VAC UNIT; FUEL PUMP TESTER; TIMING ADVANCE UNIT EXHAUST CONDENSER AND WIRING JUNCTION UNIT.
POSITIVE DISPLACEMENT SAMPLER	OLSON CVS 435-R3	7.5-hp, 4-SPEED, FLOW RATES OF 150, 225, 300, AND 400 cfm, 4 BLACK TEDLAR BAGS AND 40 FEET OF 4-in.-DIAMETER FLEXIBLE LEAKPROOF STAINLESS STEEL TUBING.
CO GAS ANALYZER	BECKMAN 315 B	NON-DISPERSIVE INFRARED ANALYZER; STACKED CELL; 6 RANGES; ± 1% FULL SCALE ACCURACY.
CO_2 GAS ANALYZER	BECKMAN 315 B	NON-DISPERSIVE INFRARED ANALYZER; 3 RANGES; ± 1% FULL SCALE ACCURACY.
HC DETECTOR	BECKMAN 400	FLAME IONIZATION DETECTOR; 4 RANGES PLUS CONTINUOUS ELECTRICAL SPAN ADJUSTMENT; ± 1% FULL SCALE ACCURACY.
NO_x GAS ANALYZER	T.E.C.O. 10A	CHEMILUMINESCENCE ANALYZER; 8 RANGES; ± 1% FULL SCALE ACCURACY.

2.2.1 Design of Vehicle Exhaust Sampling and Introduction System

An exhaust sampling system was designed for diverting a fixed amount of auto exhaust into the smog chamber during a test cycle. As shown in Figure 4, a concentric sampling tube was added to the CVS system which allowed for a fraction of the exhaust gas to be admitted into the smog chamber following mixing with dilution air. A Sutorbilt 4LXB contamination-free positive displacement gas pump driven by a 3 hp 1750 RPM motor was used to divert various amounts of the exhaust into the chamber. Under normal operating conditions, the residence time of the exhaust gases in the introduction system was approximately 0.01 second so that coagulation of the primary aerosol was minimized.

Section 3

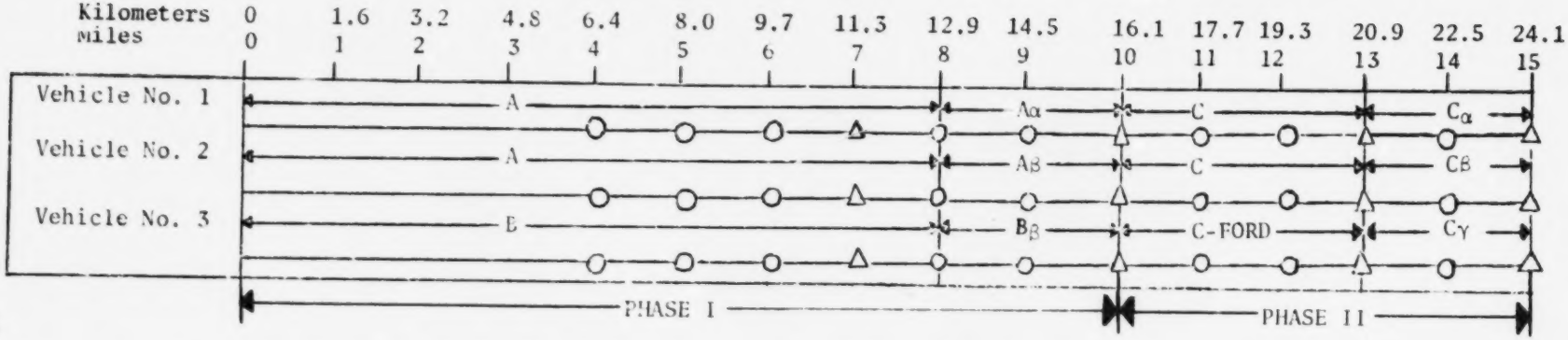
RESULTS AND DISCUSSION

3.1 Methodology Development - Phase I

The basic objective of the proposed program was to develop a methodology to determine the effects of fuels and fuel additive combustion products on atmospheric visibility. During the methodology development, the three test vehicles were independently operated on the Clayton chassis dynamometer while a portion of the auto exhaust was introduced into the smog chamber. Samples of the auto exhaust were irradiated with simulated sunlight while measurements were made of visibility, aerosol behavior, and gaseous constituents in the chamber. A wide range of experimental variables were tested including exhaust dilution ratio, effects of relative humidity, added SO_2, added HC, and the influence of natural nuclei on visibility. The test schedule for distance accumulation and emissions analyses is shown in Figure 5. Note that after the completion of Phase I tests, i.e., 16,100 km (10,000 miles), all cars began using the EPA reference fuel; at that time, Car C was replaced by a catalyst-equipped 1973 Ford Galaxie provided by the EPA.

The experiments and concomitant results which form the basis for the methodology devised in this study are described in detail in this section.

FIGURE 5. REVISED VEHICLE EMISSION TEST SCHEDULE



LEGEND

1. ○ = CONDITIONING TEST (SINGLE TEST)
2. Δ = REPRODUCIBILITY DEMONSTRATION TESTS (TRIPLICATE TESTS)
3. A = INDOLENE 0
   B = INDOLENE 0 + 0.5 GM/GAL TEL
   C = EPA REFERENCE FUEL
4. a = CHEVRON F-310
   β = ETHYL CI-2
   γ = 0.1% SULFUR

NOTES:

1. AN UNSPECIFIED NUMBER OF PRELIMINARY TESTS WILL BE PERFORMED DURING THE FIRST 11,300 km (7,000 MILES).
2. EACH ENGINE WILL BE CLEANED AND A NEW EXHAUST SYSTEM INSTALLED AFTER THE FIRST 16,100 km (10,000 MILES).
3. OPERATION OF VEHICLE #3 WAS TERMINATED AT 16,100 km (10,000 MILES) AND REPLACED WITH A CATALYST-EQUIPPED CAR.

3.1.1 Vehicle Conditioning and Emission Analysis

After initial delivery of the three Chevrolet test vehicles, Cars A and B were operated on Amoco Indolene fuel containing 13.2 mg lead per liter (0.05 gm lead per gallon) while Car C was operated on the same base stock fuel but with 132 mg lead per liter (0.5 gm lead per gallon). Approximately 1,600 km (1,000 miles) were accumulated on each vehicle every three weeks. For the first 12,875 km (8,000 miles), methodology and exhaust emissions analyses were performed at 1,600 km (1,000 mile) intervals using the basic fuels without additivies. Following the emissions tests at 12,875 km (8,000 miles), Ethyl CI-2 (132 mg/liter) and Chevron F-310 (2 ml/liter) were introduced into the test fuels as additives, and mileage accumulation was continued. After the 16,100 km (10,000 miles) point was reached and the triplicate tests were completed, the engines were disassembled and cleaned, followed by a new conditioning series using the EPA reference fuel. The later tests, which comprised Phase II testing, are described in a subsequent section of this report.

Results of the emissions analyses for the three test vehicles during the first 16,100 km (10,000 miles) are shown in Figures 6, 7, and 8. The data show HC, CO, and NO_x emissions respectively as functions of mileage accumulation. The data in Figure 6 indicate relatively stable HC emissions for Cars A and B for the first 12,876 km (8,000 miles) followed by a slight upward trend in these emissions. For the most part, however, the HC emissions for Car A remained basically the same throughout the first 16,100 km (10,000 miles). Car C, on the other hand, showed the highest level HC emissions and experienced a steady rise in the HC level until reaching stability at the 12,875 km (8,000 miles) point giving approximately 1.5 gm HC/km (2.4 gm HC/mile).

Carbon monoxide and oxides of nitrogen emissions, Figures 7 and 8, show consistent trends for all three vehicles. The data do not appear to have been affected by the introduction of additives. As with HC, Car C had the highest level of CO emissions but slightly lower than average NO_x levels. After the first 11,260 km (7,000 miles), all three cars had relatively stable NO_x emissions. Repeatability of test results was somewhat better for each vehicle during the second triplicate emissions series.

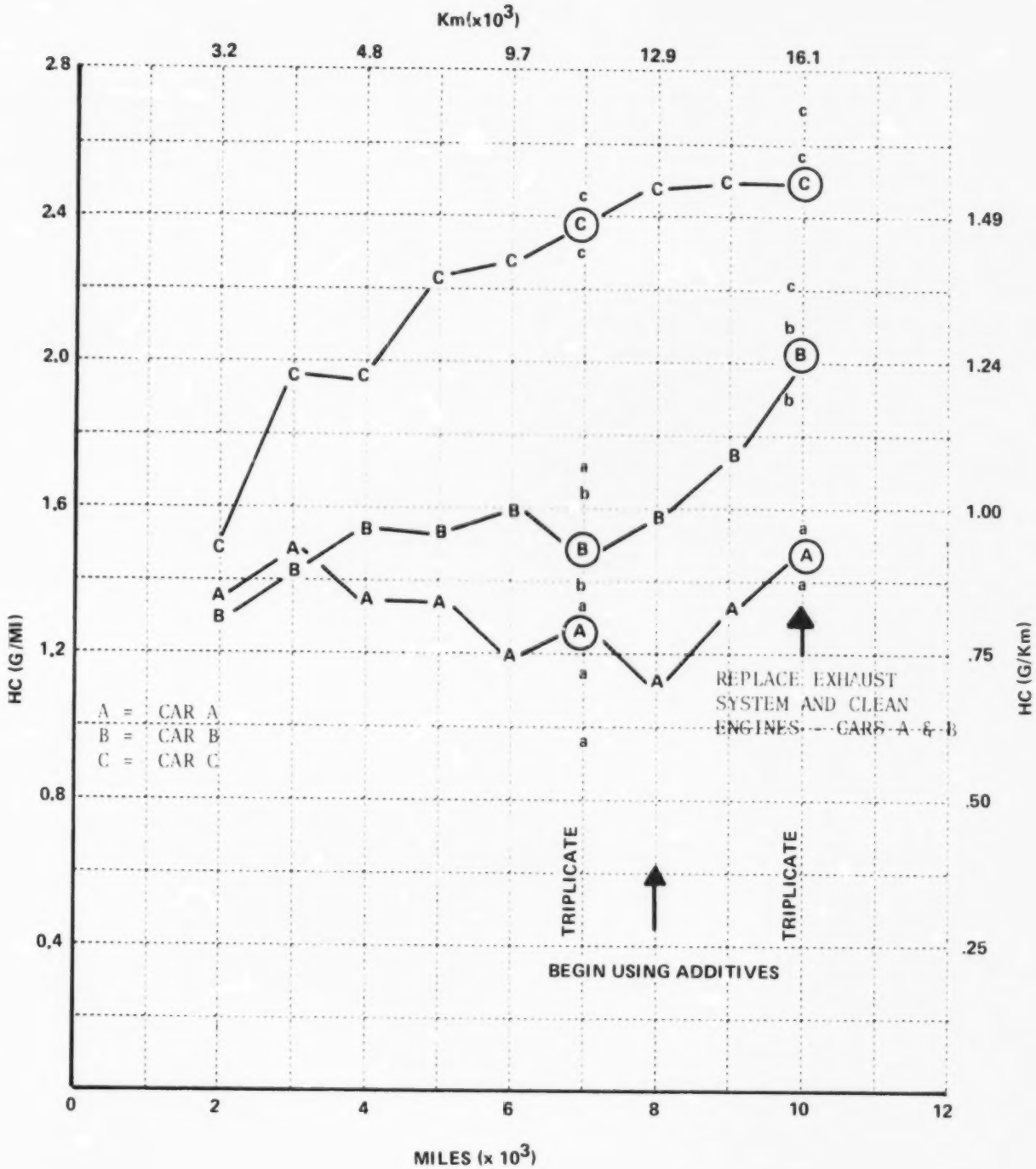


Figure 6 HYDROCARBON EMISSIONS VS KILOMETERS (MILES) ACCUMULATED ON VEHICLES

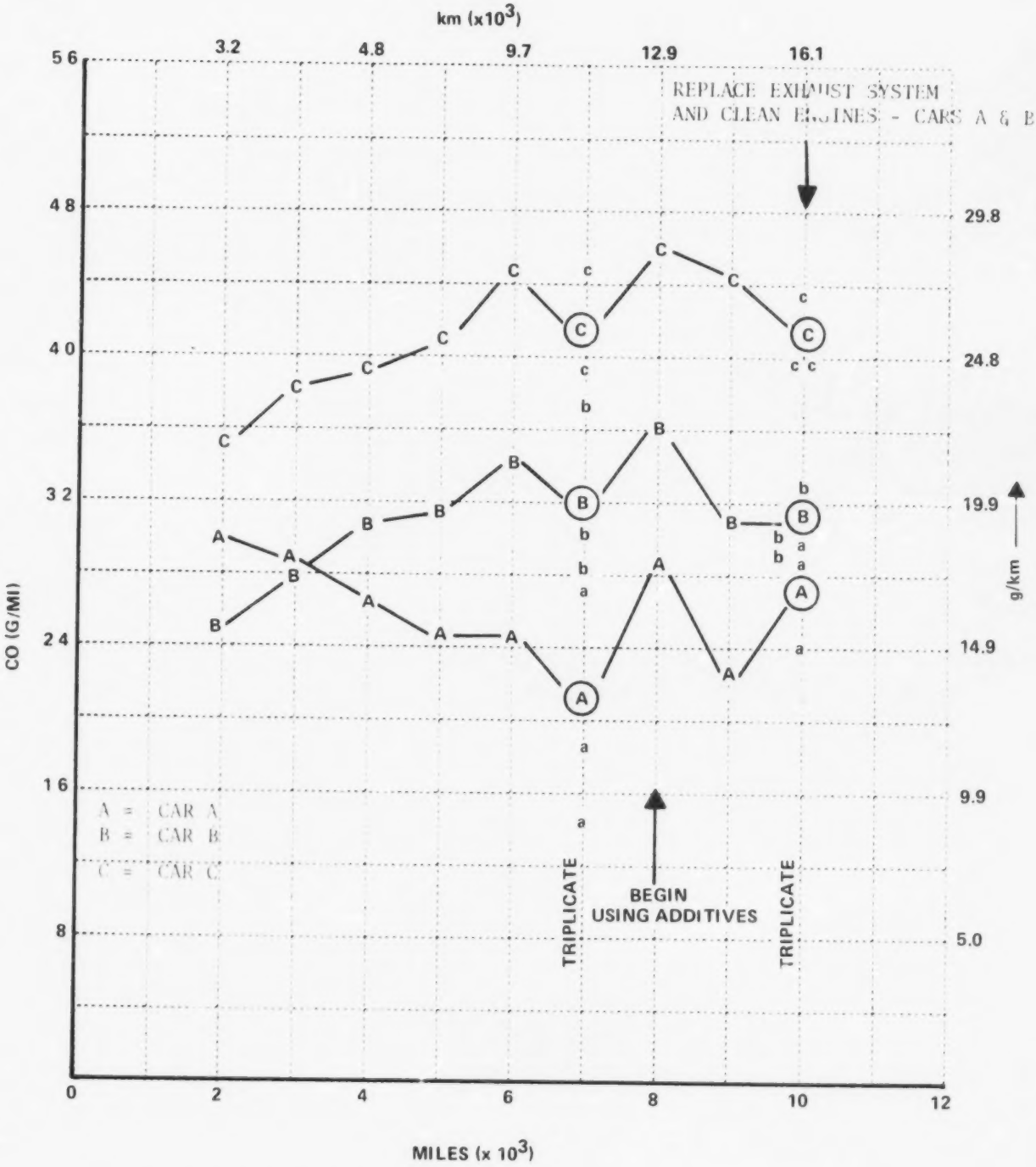


Figure 7 CARBON MONOXIDE EMISSIONS VS KILOMETERS (MILES) ACCUMULATED ON VEHICLES

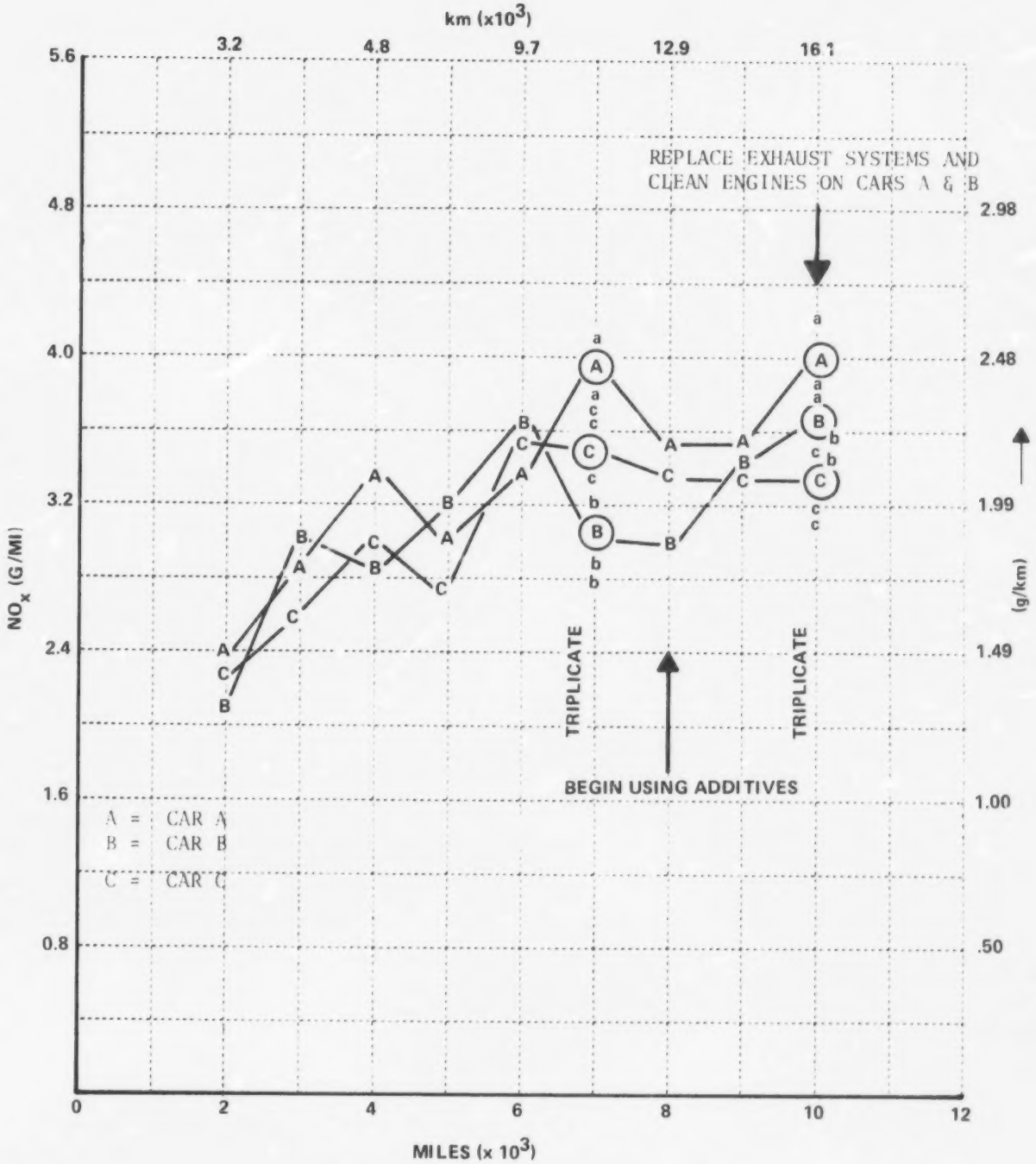


Figure 8 NO_x EMISSIONS VS KILOMETERS (MILES) ACCUMULATED ON VEHICLES

These data were particularly valuable in interpreting results during the methodology repeatability tests. For example, it was later shown that even small amounts of excess hydrocarbon had an adverse effect on the final visibility in the smog chamber. Thus, the high HC and low NO_x levels for Car C were found to be responsible for the low visibilities observed after irradiation and not necessarily the fact that leaded fuel was being used. (It is possible that the leaded fuel influenced the HC emissions for Car C and thus indirectly affected visibility; however, this cannot be established without comparative tests with the same car using non-leaded fuel.)

3.1.2 Effects of Dilution Ratio, Relative Humidity, Variations in Natural Air, Added SO_2 and Added Hydrocarbon on Test Results

Smog chamber tests were designed to study the effects of background air (i.e., filtered vs. natural air), dilution ratio, relative humidity, and added SO_2 on chamber visibility. In most experiments filtering of the air (absolute plus charcoal) was accomplished before introducing exhaust into the chamber. On occasion, background air containing natural nuclei from the rural environment was used for a test. During this stage of methodology development, the first 10 minutes of the LA-4 cycle was driven on the chassis dynamometer, while a fixed amount of auto exhaust was admitted into the chamber. Dilution ratios of 200:1, 300:1, 500:1, and occasionally 1000:1 were tested.

Visibility traces from selected experiments showing the effect of variations in natural air on test results are shown in Figure 9. For the experiments shown in Figure 9, outside air was first admitted into the chamber followed by the addition of auto exhaust at a dilution ratio of 200:1. The sample was then irradiated for up to 23 hours, while observations were made of visibility, NO_x, oxidant, total sulfur, and particle concentration.

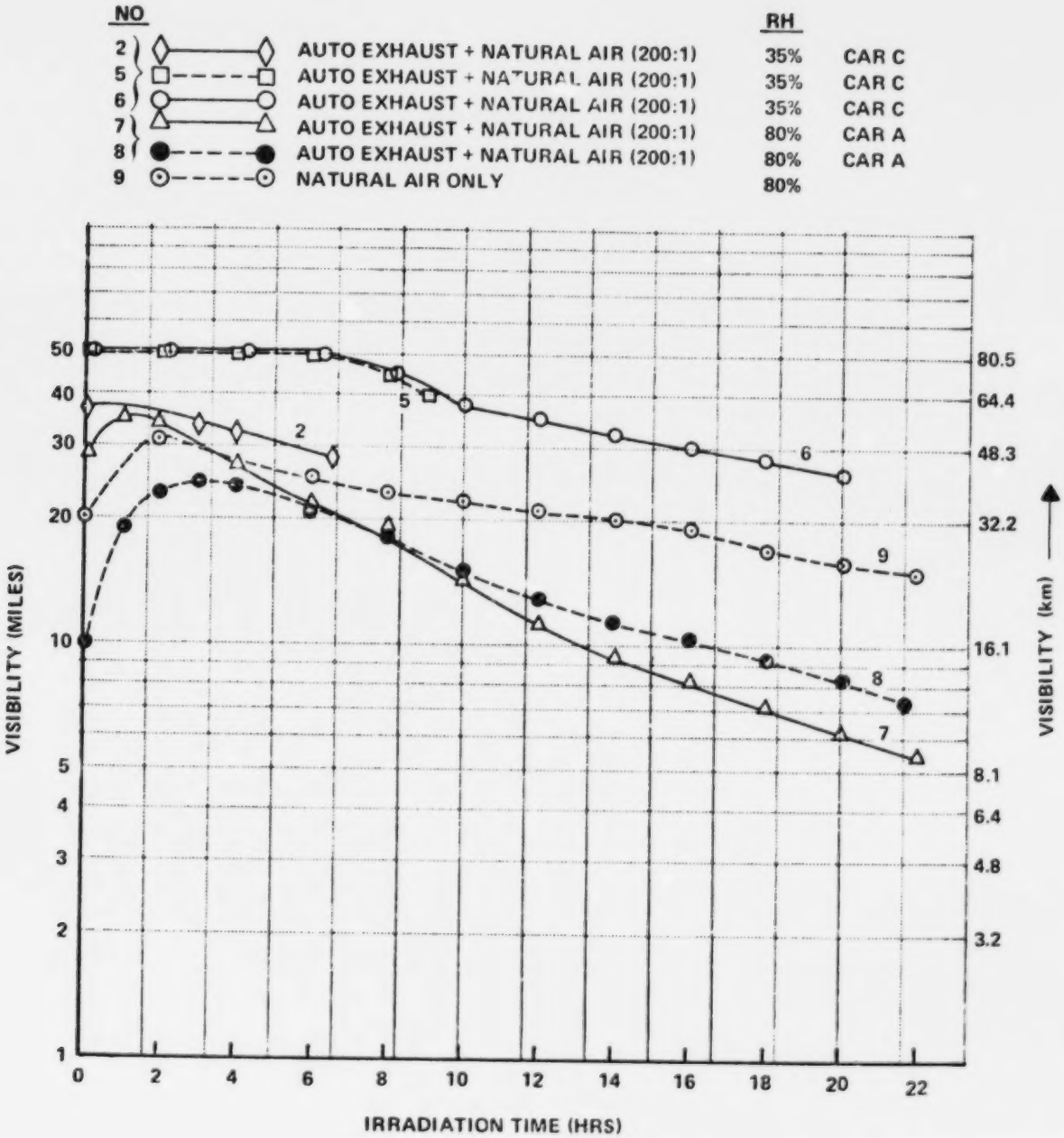


Figure 9 EFFECT OF VARIATIONS IN NATURAL AIR ON TEST RESULTS

The data in Figure 9 show that variations in the nucleus concentration and background gaseous contaminant level in the natural air produce widely different initial visibilities as well as important differences in test results. For example, a comparison of seemingly identical experiments, such as 2, 5, and 6 or 7 and 8, show poor repeatability. Despite the fact that added realism is provided by using natural air in the smog chamber, the wide variability caused in test results makes this procedure unacceptable in terms of methodology development. In all subsequent experiments, therefore, chamber air was normally filtered for several hours before the start of an experiment in order to remove particulates and trace gaseous contaminants from the atmosphere.

In Figure 10 the effect of differences in relative humidity and added SO_2 on test results is shown. Air which was first filtered thoroughly was used in these experiments and all dilution ratios were the same (i.e., 200:1). As shown by the data for run no. 4, auto exhaust plus filtered air which was irradiated for 20 hours at low humidity (~35%) resulted in only a small restriction in visibility. On the other hand, experiment 10, which represents the same test condition but high humidity (~80%), shows a much larger visibility loss with time. After 18 hours of irradiation in that experiment, visibility decreased from 80+ km (50+ miles) to approximately 29 km (18 miles). The effect of high humidity can be anticipated, of course, since any hygroscopic component of the nuclei in the chamber will deliquesce and enlarge if there is sufficient moisture available.

The combined effects of high humidity and added SO_2 can be seen by comparing experiments 11 and 12. Here, the same dilution ratios were used, but approximately 0.8 ppm SO_2 was added to each system shortly before introducing auto exhaust into the chamber. As shown, the addition of sulfur dioxide had a substantial effect on the visibility within the test environment. In the high humidity case (experiment 12), there was an effect even before irradiation was started. This probably was the result of a dark reaction of the SO_2 followed by enlargement of the H_2SO_4 aerosol at high humidity. Once the lights were turned on, increased photooxidation of SO_2 occurred causing the production of significant additional light scattering aerosol. After 22 hours of irradiation, the visual range had dropped to 3.9 km (2.4 miles) in this experiment.

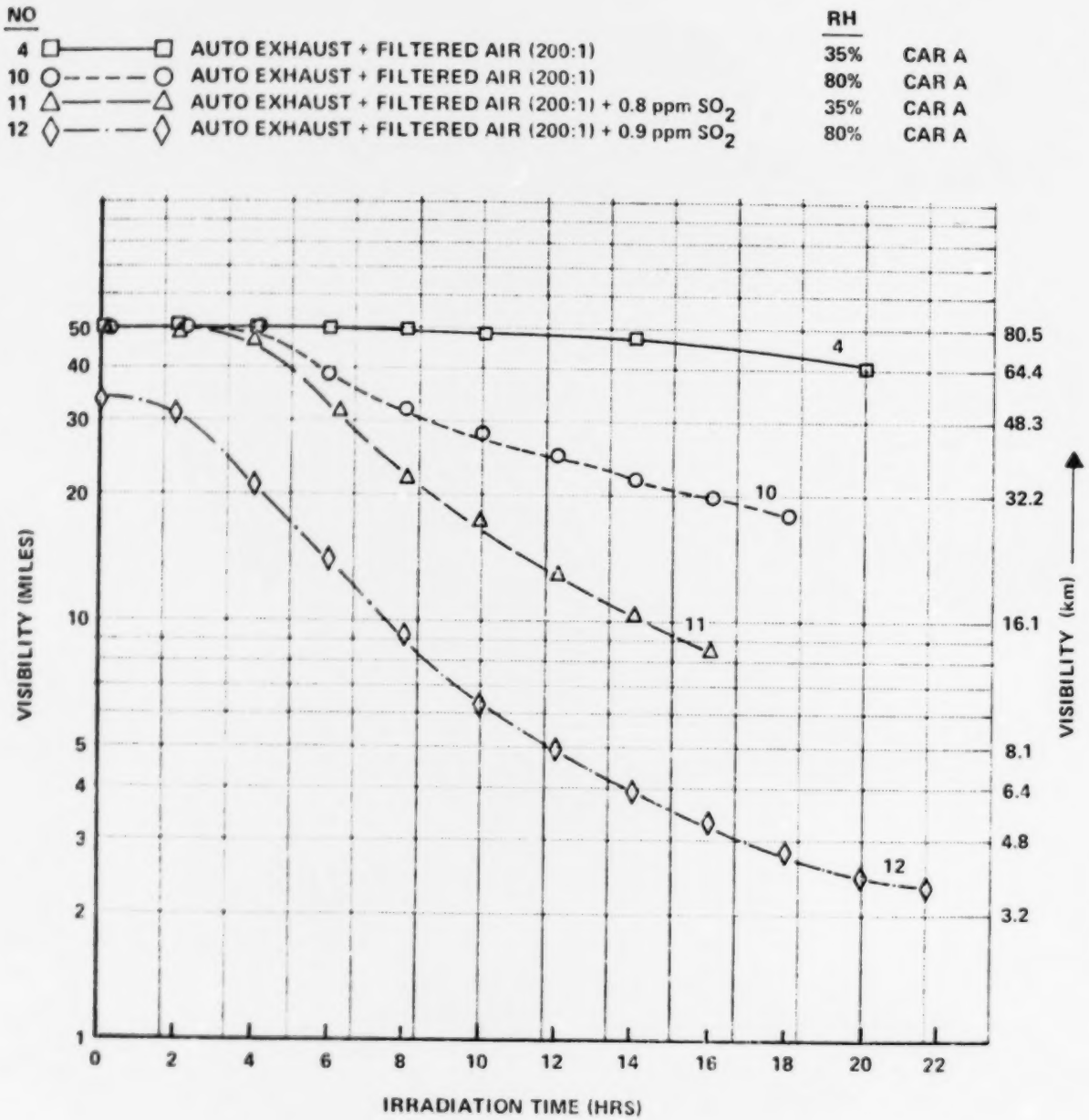


Figure 10 EFFECT OF RELATIVE HUMIDITY AND ADDED SO_2 ON TEST RESULTS

Because of the dominant effect which high humidity had on test results, it was decided that subsequent experiments would be performed at lower humidities in the range of 30±10% RH. Smaller dosages of SO_2, more typical of levels found in natural urban atmospheres, were also considered desirable.

Results showing the effect of differences in dilution ratio and additional comparisons of the effect of added SO_2 on visibility are shown in Figure 11. These experiments show that in the absence of any added SO_2 a dilution ratio not greater than 200:1 is required to produce even slight visibility losses after irradiation (e.g., experiments 4 and 13). With the addition of SO_2 (i.e., 0.12 ppm) to the system, dilution ratios of approximately 500:1 produce some visibility restriction. At a dilution ratio of 1000:1, no visibility loss at all is observed even in the presence of added SO_2.

During the course of these experiments, it was noted that aerosol formation was closely tied to the oxidation and disappearance of nitric oxide (NO) from the system. This observation, while important in terms of understanding the mechanisms of particle formation, was a complicating factor in the methodology development. For example, auto exhaust from the test vehicles, when operated in accordance with the Federal test schedule, is inherently high in nitrogen oxides and relatively low in reactive hydrocarbons. Under these conditions, the oxidation of NO proceeds slowly and aerosol formation is suppressed. On the other hand, in the presence of larger concentrations of reactive hydrocarbon, the oxidation of NO and the formation of ozone is greatly accelerated and particle formation mechanisms are favored. This effect is illustrated in Figure 12 where visibility data for several experiments are shown. In the one case, 2 cc (0.7 ppm) of hexene-1 was added to a system containing 2.1 ppm NO and a trace amount of SO_2. The large inhibiting effect of nitric oxide on the formation of light scattering aerosol is obvious from these results in which visibility never dropped below 80+ km (50+ miles) in the case where NO was present. The data are compared with a similar test in which only background levels of NO were present. In this case, appreciable light scattering aerosol was formed, and substantial visibility losses were observed during the course of the experiment. A third case is illustrated in which

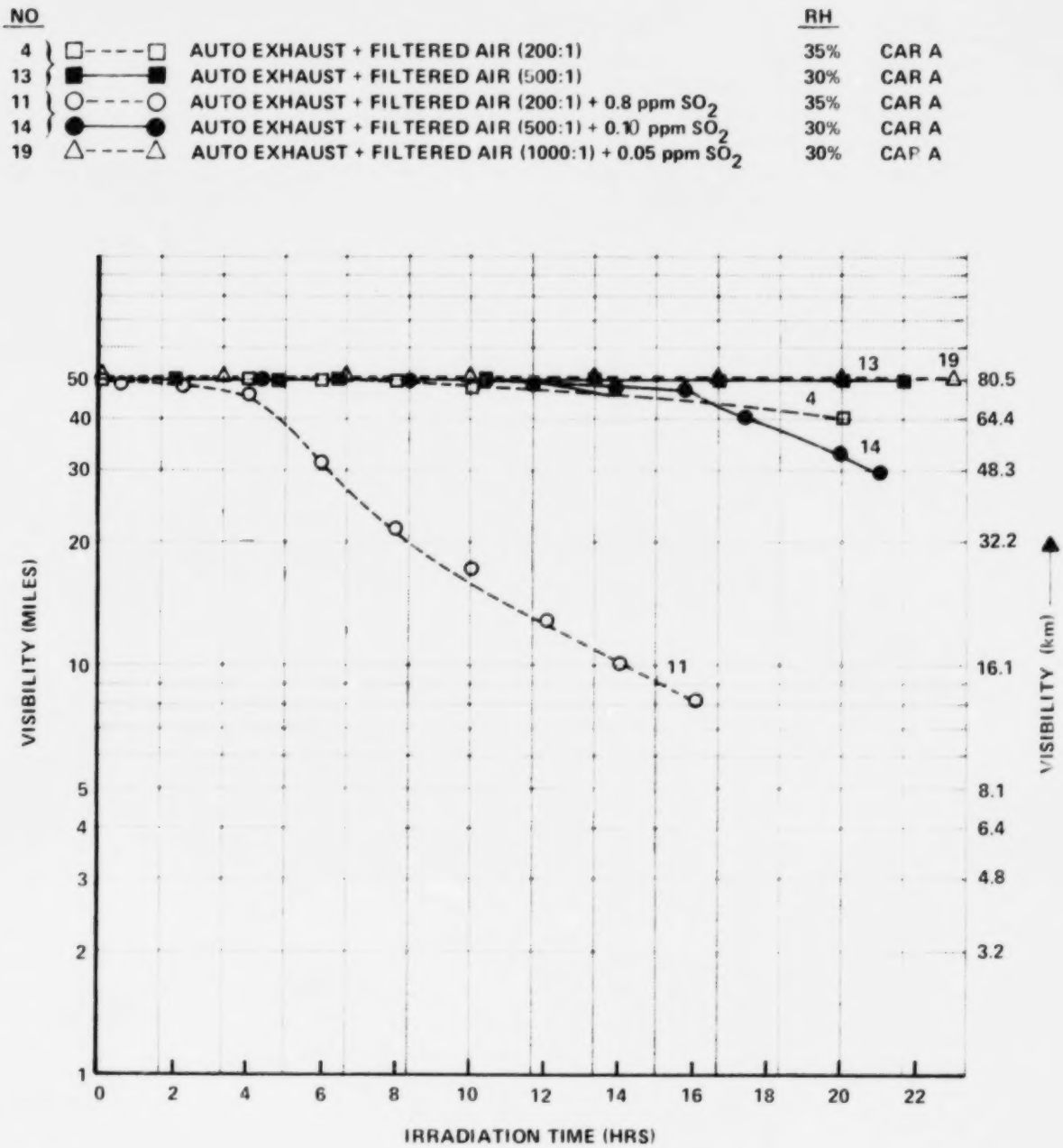


Figure 11 EFFECT OF DILUTION RATIO AND ADDED SO_2 ON TEST RESULTS

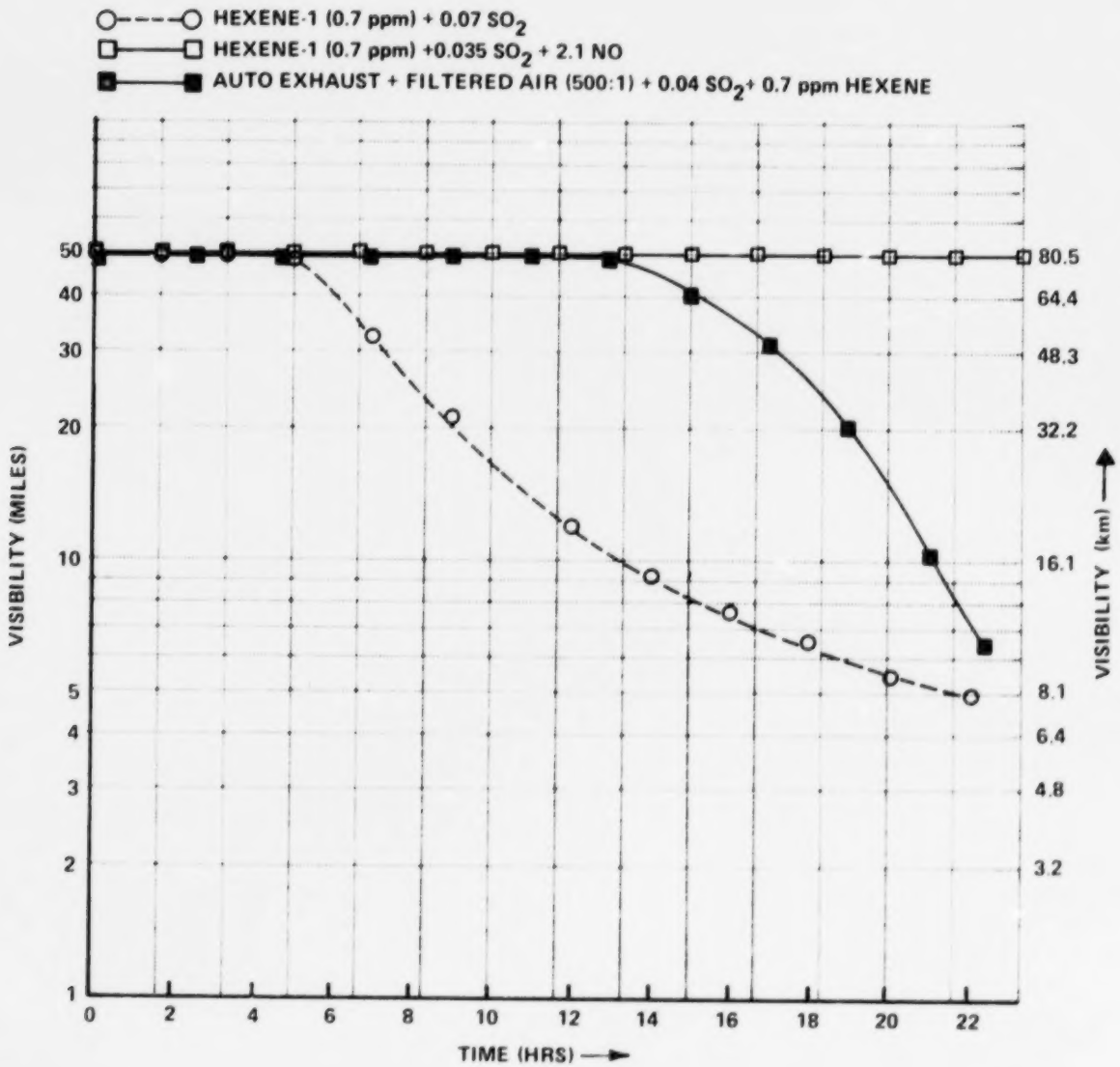


Figure 12 COMPARISON OF HEXENE-1•SO_2 IRRADIATION WITH AND WITHOUT THE ADDITION OF NO

2 cc (0.7 ppm) hexene was added to a 500:1 auto exhaust + filtered air system with 0.04 ppm added SO_2. Here approximately 13 hours elapsed while the NO was being oxidized out of the system. After that time there was rapid formation of ozone and of light scattering aerosol as indicated by substantial visibility losses. It was determined following these tests that as part of the methodology repeatability demonstration, an additional experiment would be performed for each car. In these tests, 3 cc of the low-lead or non-leaded fuel would be added to the exhaust gas + SO_2 system as an evaporative emission. The added HC was expected to provide a more realistic HC/NO_x ratio of approximately 3:1 instead of the 1:1 ratio that normally was observed.

In summary, then, the following test conditions were chosen as a result of the methodology development phase of the program.

Dilution Ratio: 300:1
Relative Humidity: 30±10%
Added SO_2: 0.05 ppm
Irradiation Time: 23 hours
Temperature: $24^{o}\pm5^{o}C$ ($75\pm10^{o}F$)

One additional test was performed for each of the vehicles in which 3 cc of the test fuel was added to the chamber as an evaporative emission.

3.1.3 Repeatability Tests - Phase I

Triplicate repeatability tests of the Phase I methodology were performed on each test vehicle after the 12,900 and 16,100 km (8,000 and 10,000 mile) accumulation points. Following tests at the 12,900 km (8,000 mile) point, the additives CI-2 and Chevron F-310 were introduced into the test fuels, and distance accumulation was continued. The repeatability tests involved admitting auto exhaust into the large smog chamber at a 300:1 dilution with air, adding 0.05 ppm SO_2 and irradiating the sample for 23 hours.

Results of methodology repeatability tests are summarized in Table II and compared with test data acquired prior to the addition of additives to the test fuels. Good reproducibility of test results was achieved for Cars B and C, but not for Car A. In fact, during the performance of the second test series at 16,100 km (10,000 miles), the variability in Car A test data was particularly large. Careful inspection of the data showed that variations in engine performance were causing large differences in the HC level within the chamber which, in turn, produced significant changes in the final observed visibility. After completing several experiments, measurements of initial HC in the chamber were made using a Beckman flame ionization detector from the vehicle emissions laboratory. These measurements allowed us to establish the HC/NO ratio in the chamber at the start of each experiment and to correlate this ratio with the final visibility in the chamber. The close correlation is illustrated in Figure 13, showing essentially an exponential dependence of final visibility on the initial HC/NO ratio inherent in the vehicle exhaust. The dashed line shows the effects of further increases in the initial HC/NO ratio as a result of introducing evaporative emissions into the chamber.

In terms of final visibility within the smog chamber, the excellent repeatability of test results for Cars B and C (although fortuitous) was the result of nearly identical concentrations of exhaust emissions being introduced into the chamber during the respective test runs. In all cases, variations in emissions, especially for NO, were observed to correlate closely with extreme changes in relative humidity. For Car A tests, the exhaust HC/NO ratio varied from 0.61 to 1.13; consequently, the observed final visibility for these tests also varied over a wide range. On warm, humid days the NO emissions were predictably somewhat less giving a high HC/NO ratio and lower final visibilities in the chamber. During the winter, weather was less of a factor since the relative humidity was always low once the outside air reached room temperature. (Because of these observed changes in engine emissions as a function of relative humidity, special provisions were made to control the carburetor air intake for the Phase II tests involving the EPA reference fuel. These tests are discussed in the next Section.)

TABLE II.

METHODOLOGY REPEATABILITY TESTS - CARS A, B & C

Test		Condition	^{o}C T	RH %	NO_i ppm	NO_f ppm	HC ppmC	Initial HC/NO	Visibility in Kilometers (miles) after 23 hours irradiation April 16,100 km (10,000 mi)		Feb. 12,870 km (8,000 mi)	
Car A	#18	300:1 + 0.05 SO_2	25.5	46%	2.94	1.30	3.15	1.07	35.1		17.2	
	#19	"	25.0	32%	4.10	2.20	2.50	0.61	61.1	42.5±19	29.8	30.9±2.1
non-	#20	"	25.0	41%	3.78	1.90	2.05	0.79	46.7	(26.4±12)	33.0	(19.2±1.3)
lead	#21	"	26.1	55%	2.91	1.21	3.30	1.13	27.3			
fuel	#22	300:1 + 0.05 SO_2 + 3 cc HC	26.7	43%	3.58	1.28	8.05	2.25	11.3		12.7	
+ F-310												
Car B	#11	300:1 + 0.05 SO_2	19.4	39%	3.45	1.64	3.60	1.04	35.1		30.6	
	#13	"	21.7	31%	3.55	1.78	3.55	0.97	36.8	31.9±5.0	36.7	33.5±3.2
non-	#15	"	25.3	40%	3.47	1.62	3.90	1.13	27.0	(19.8±3.1)	33.0	(20.8±2.0)
lead	#16	"	26.7	36%	3.30	1.35	3.75	1.13	28.5			
fuel	#17	300:1 + 0.05 SO_2 + 3 cc HC	25.5	40%	3.27	0.90	8.85	2.70	9.6		12.9	
+ CI-2												
Car C	#23	300:1 + 0.05 SO_2	21.1	36%	3.68	1.57	5.25	1.43	15.1		28.2	
	#24	"	23.9	48%	3.20	1.13	5.25	1.64	12.4	14.3±1.9	29.0	26.5±4.0
low-	#25	"	24.4	49%	3.32	1.29	5.00	1.51	15.8	(8.9±1.2)	22.5	(16.5±2.5)
lead	#26	300:1 + 0.05 SO_2 + 3 cc HC	28.3	51%	2.97	--	10.8	3.63	5.6			
fuel + CI-2												

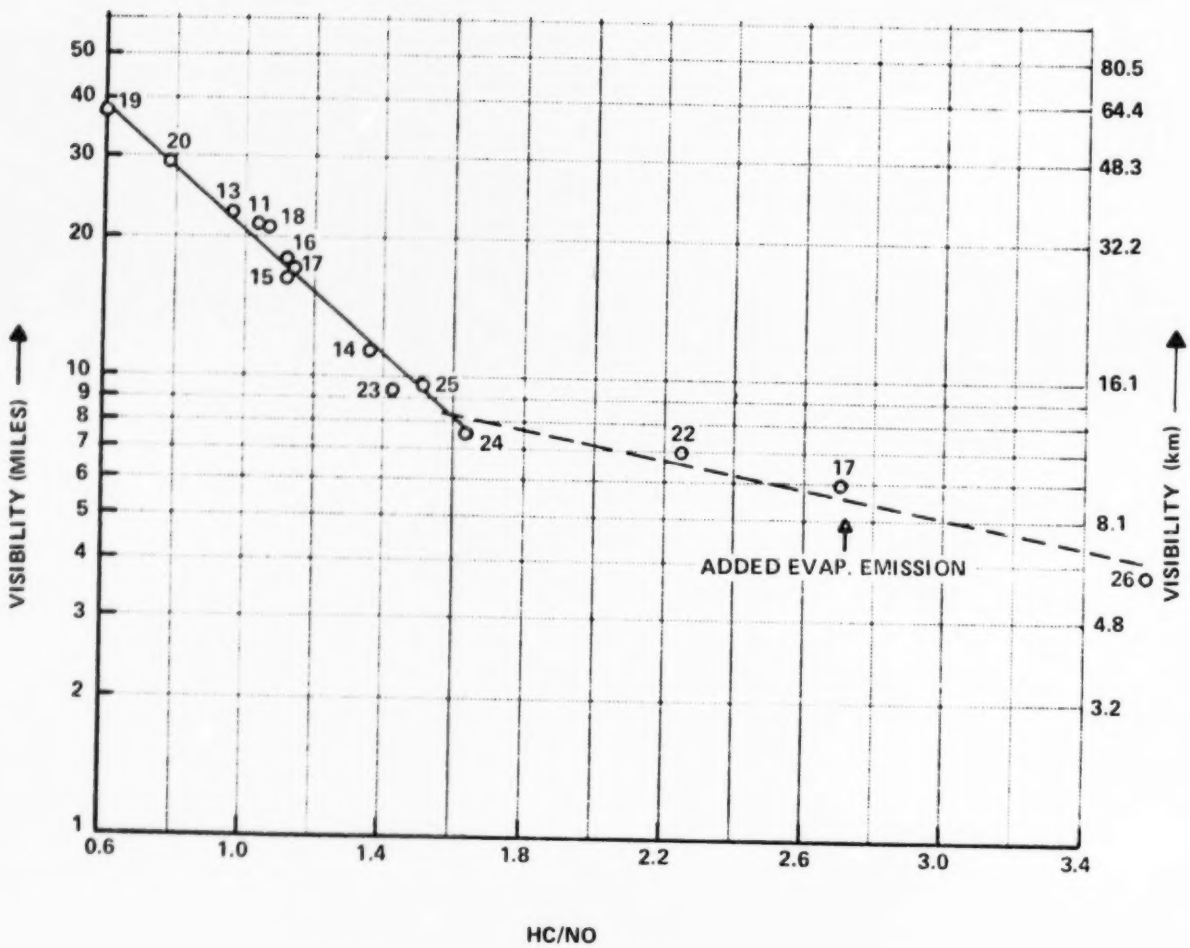


Figure 13 FINAL VISIBILITY IN SMOG CHAMBER VS INITIAL HC/NO RATIO OF EXHAUST EMISSIONS (TEST NUMBER SHOWN ADJACENT TO EACH DATA POINT)

As a result of the aforementioned variability in engine performance, no meaningful comparisons of additive and non-additive tests could be made for the Car A data. Results for Car B during the two test series were essentially unchanged leading to the conclusion that there was no effect of the additive within the experimental variability of the data. Final visibility data for Car C were significantly lower during the additive test series. To conclude that there was an adverse effect due to the additive is not warranted, however, since the observed low visibility could have been predicted based on the Car C HC/NO data alone. It is not obvious, however, whether the comparatively high HC emissions for Car C were affected by the additive or were inherent in the engine performance. It may be noted that even in the absence of CI-2, Car C with low-lead fuel gave somewhat lower visibilities during the additive-free test series than Cars A and B which were operated on lead-free fuel.

One observed effect of the additive Ethyl CI-2 in combination with the low-lead fuel (Car C) was that the emission of primary particulates from Car C produced an immediate visibility loss in the smog chamber, even before the lights were turned on. This can be seen in Figure 14 in which visibility in the smog chamber is plotted against irradiation time in hours. Note that the initial visibilities lie in the range of about 50 to 70 km (32 to 45 miles) after introducing exhaust into the chamber. All additive-free tests for Car C and all tests for Cars A and B show no initial visibility losses for a 300:1 dilution ratio. The data for Cars A and B showing visibility vs. time are plotted in Figures 15 and 16. The very pronounced effect of the added evaporative emission on final visibility can also be noted in these figures.

Several additional experiments were performed to determine the effects of primary particulates on visiblity within the smog chamber after irradiation. Three types of experiments were performed. In the initial test, auto exhaust (dilution ratio 300:1) plus 0.05 ppm SO_2 was irradiated for 23 hours. In the second experiment, all primary particulates in the auto exhaust were removed by absolute filtration before turning the lights on. Exactly 0.05 ppm SO_2 was then added to the system, and the exhaust gas plus SO_2 mixture was irradiated for 23 hours. A final experiment involved the introduction

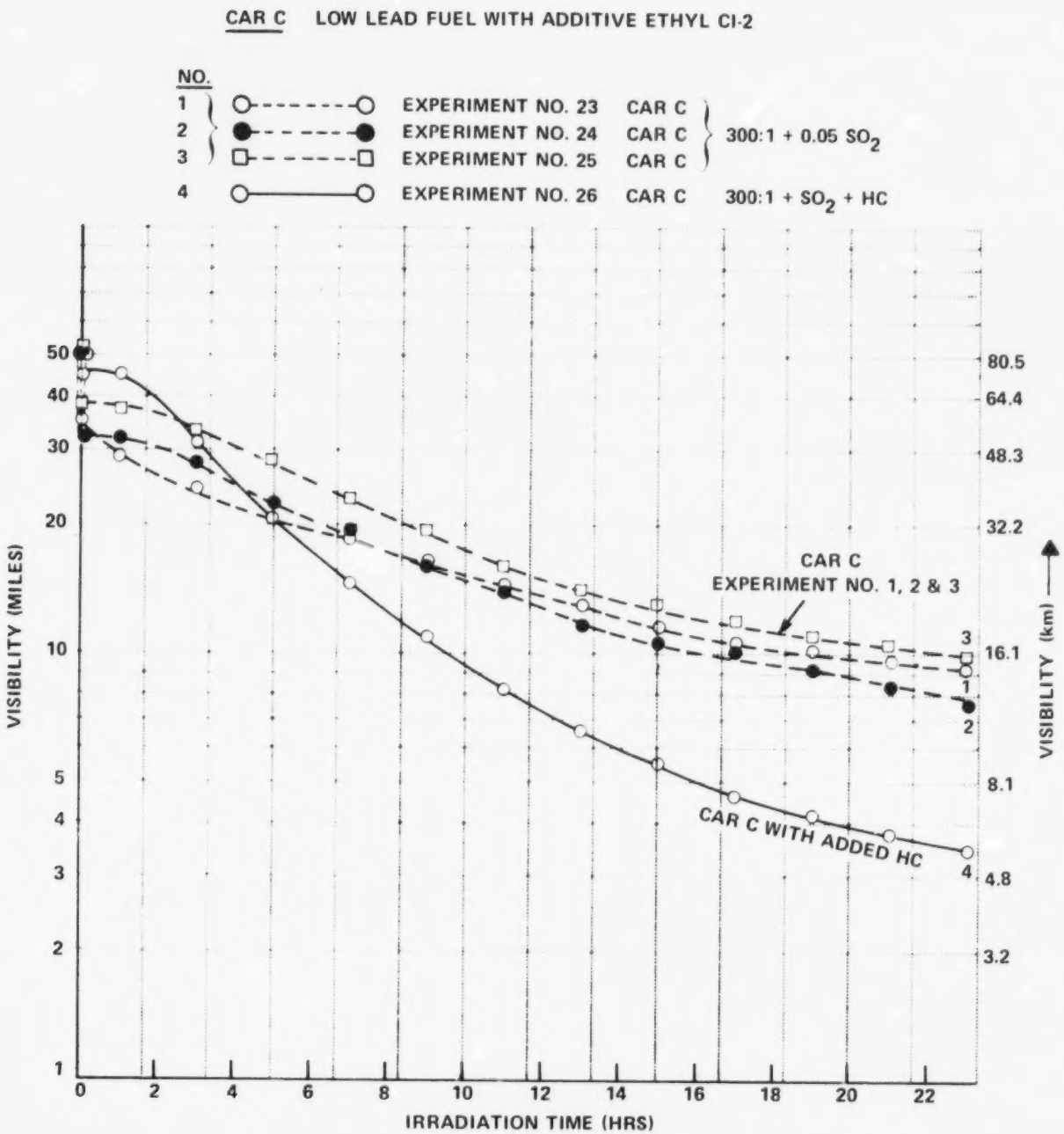


Figure 14 REPEATABILITY TESTS FOR 300:1 DILUTION PLUS 0.05 ppm ADDED SO_2

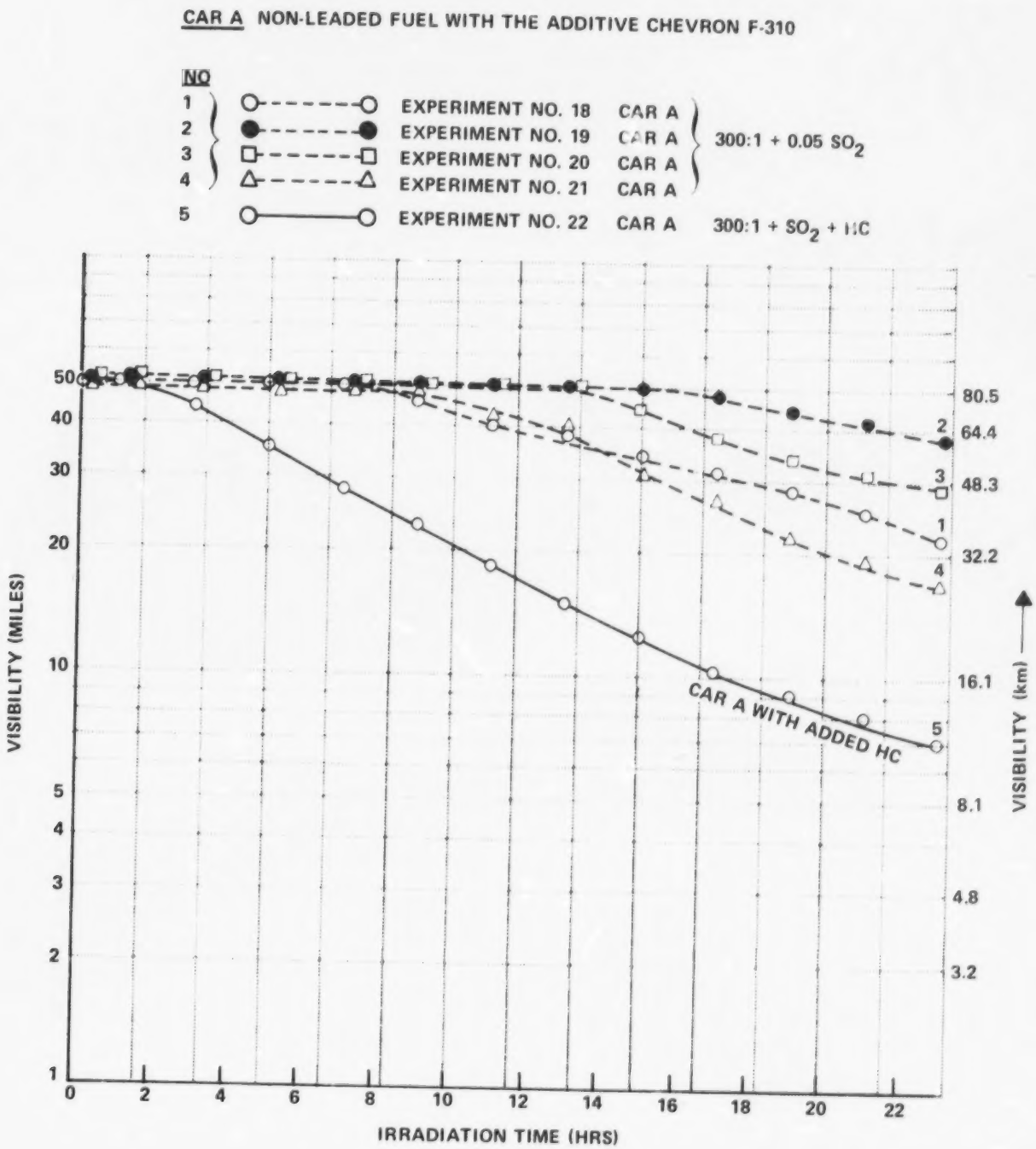


Figure 15 REPEATABILITY TESTS FOR 300:1 DILUTION PLUS 0.05 ppm SO_2

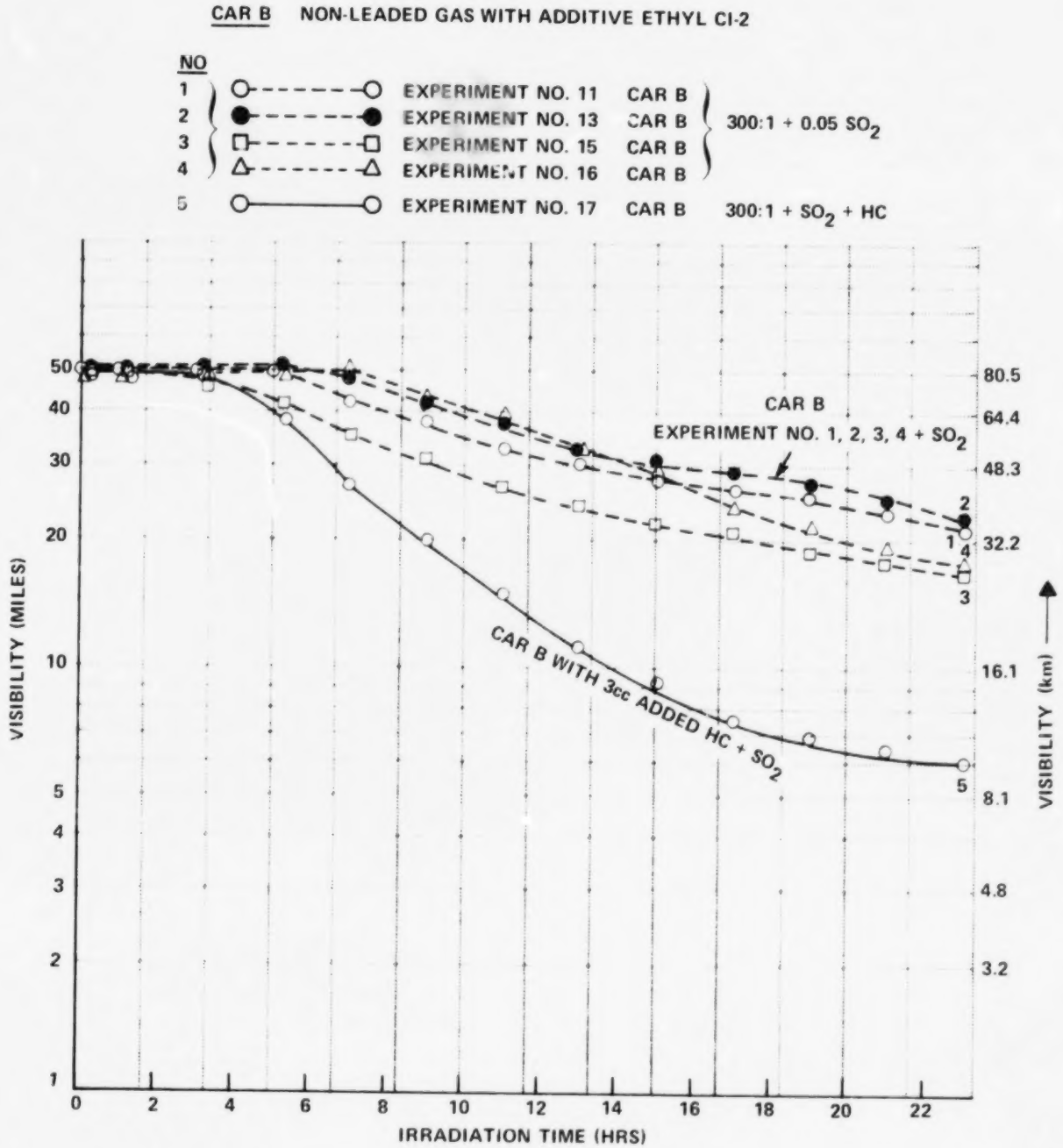


Figure 16 REPEATABILITY TESTS FOR 300:1 DILUTION PLUS 0.05 ppm ADDED SO_2

of equivalent amounts of HC plus NO into clean filtered chamber air in order to simulate auto exhaust pollutant levels comparable to those used in previous tests. The results are shown in Figure 17 in which visibility is plotted as a function of irradiation time for each of the tests.

In test number 1 (auto exhaust with primary particulates + 0.05 ppm SO_2), there was an immediate reduction in visibility after introducing the exhaust products into the chamber. This effect is typical for Car C which was being operated on low-lead fuel with the additive Ethyl CI-2. After irradiation for 21 hours, the smog chamber visibility dropped to 5.5 km (3.4 miles), a value which is consistent with the methodology tests. In experiment 2 (i.e., filtered auto exhaust + SO_2), a much lesser visibility loss was noted. In fact, the minimum visibility of about 29 km (18 miles) was observed after 17 hours of irradiation, followed by a slow improvement to 40 km (25 miles) during the next six hours of the experiment. Aerosol size distribution analysis for these two experiments show that the surface concentration of particulates at the end of experiment 1 was 2.8×10^4 $\mu m^2/cm^3$ and at the completion of experiment 2 about 1.2×10^4 $\mu m^2/cm^3$ or less than half as much. This difference in surface concentration is sufficient to account for the observed differences in visibility. (The amount of scattered light is directly proportional to the cross sectional area of the particles.) Visibility data for a third test involving HC + NO + SO_2 gases is also shown in Figure 17. For this case, only a modest reduction in visibility was noted after lengthy irradiation.

These test results demonstrate that primary particulates play an important role in the initial and final visibilities noted in the smog chamber. Furthermore, the tests show that irradiations of HC+NO+SO_2 mixtures comparable to those found in auto exhaust do not produce equivalent visibility losses. It is concluded that in order to examine the effects of fuels and fuel additive combustion products on atmosphere visibility natural auto exhaust containing primary particulates must be used.

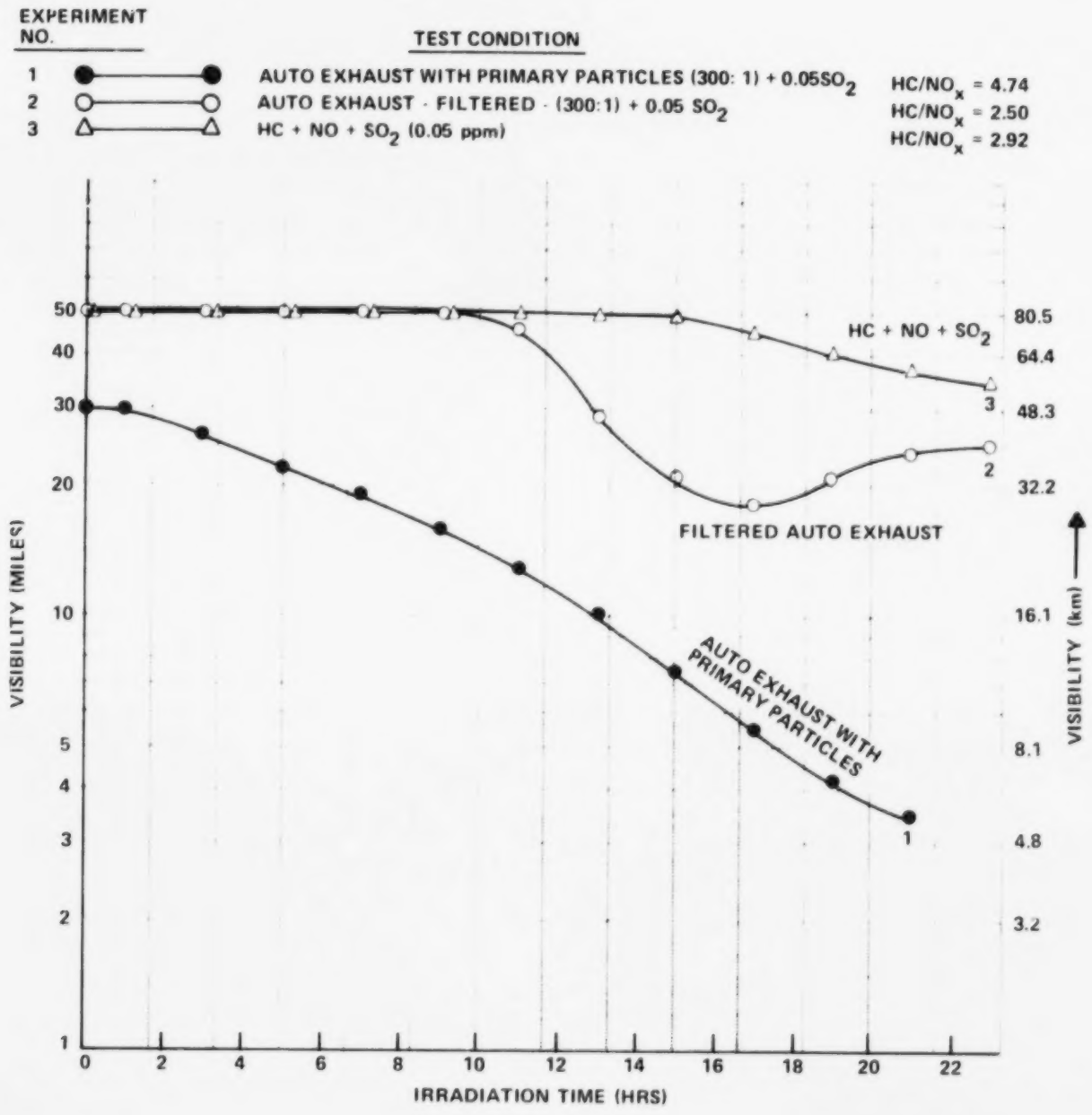


Figure 17 EFFECTS OF PRIMARY PARTICULATES ON TEST RESULTS - CAR C

3.1.4 Summary of Phase I Test Results

From the analysis of data acquired during the first phase methodology development and repeatability tests, the following conclusions can be drawn:

(1) The effects on visibility in a 590 m^3 (20,800 ft^3) smog chamber of the additives Ethyl CI-2 and Chevron F-310 are small compared to the effects brought about by natural variations in engine performance.

(2) The combined effect of Ethyl CI-2 with a low-lead fuel had a marked influence on the initial visibility observed in the smog chamber. No other combination of fuels or additives showed this effect.

(3) The final visibility achieved after irradiation of a 300:1 exhaust gas-filtered air mixture with 0.05 ppm added SO_2 is closely correlated with the initial HC/NO ratio in the chamber. In fact, the correlation is so good that final visibilities can be accurately predicted from an initial measurement of total HC and nitrogen oxide in the chamber.

(4) Besides having the expected effect of reducing initial visibility in the smog chamber, primary particulates in auto exhaust were found to play a dominant role in the long-term visibility losses as well (i.e., 23 hours irradiation).

It should be noted that the basic objective of this program was methodology development. No attempts were made to perform a sufficient number of tests on any single system to permit rigorous statistical assessment of the effects of specific fuels or additives on visibility. The above summary of test observations serve only to demonstrate the efficacy of the methodology derived. Some test procedure shortcomings are quite evident. Methodology modifications were therefore again emphasized in Phase II of the program. Humidity control on test vehicle carburetor intake air to minimize HC/NO variability on a given vehicle-fuel system was identified as an essential requirement from Phase I test results.

3.2 Methodology Tests: Phase II - EPA Reference Fuel

After completion of the Phase I triplicate emissions tests and chamber experiments at the 16,100 km (10,000 mile) point, the engine heads from the three test vehicles were removed and cleaned, and new exhaust systems were installed. By mutual agreement, Car C was dropped from the testing program and replaced by a catalyst-equipped 1973 6.55 liter (400 CID) Ford Galaxie 500 supplied by the EPA. Distance accumulation was again started on each of the cars using lead-free, low sulfur (~124 ppm) reference fuel. After 4,830 km (3,000 miles), a triplicate emission and smog chamber test series was performed on all cars followed by the addition of the additives Chevron F-310 and Ethyl CI-2 to the fuel of Cars A and B, respectively. At the same time, fuel used in the catalyst Ford was doped with sufficient thiophene to give a sulfur content of ~1,000 ppm.

Earlier difficulties in maintaining stable temperature and humidity conditions in the emissions laboratory were rectified by using a refrigeration system with reheat coils to supply controlled air to the cars during a test. In operation, refrigerated air from a one-ton air conditioner was directed through ductwork and over a series of heaters slightly ahead of the air intake of the carburetor. By regulating the amount of heat supplied to the refrigerated air within the ductwork, humidities between 30% and 80% could reliably be obtained. For our tests, the relative humidity was kept at approximately 40%.

3.2.1 Emission Analyses

Complete results of the emissions analysis for each of the test cars for Phases I and II are shown in Figures 18, 19, and 20. The tests were performed every 1,610 km (1,000 miles) with the Phase II triplicate emissions tests performed at the 20,920 and 24,140 km (13,000 and 15,000 mile) points.

In general, the Phase II hydrocarbon emissions for Cars A and B are comparable to Phase I tests and average approximately 0.9 g/km (1.5 g/mile). The

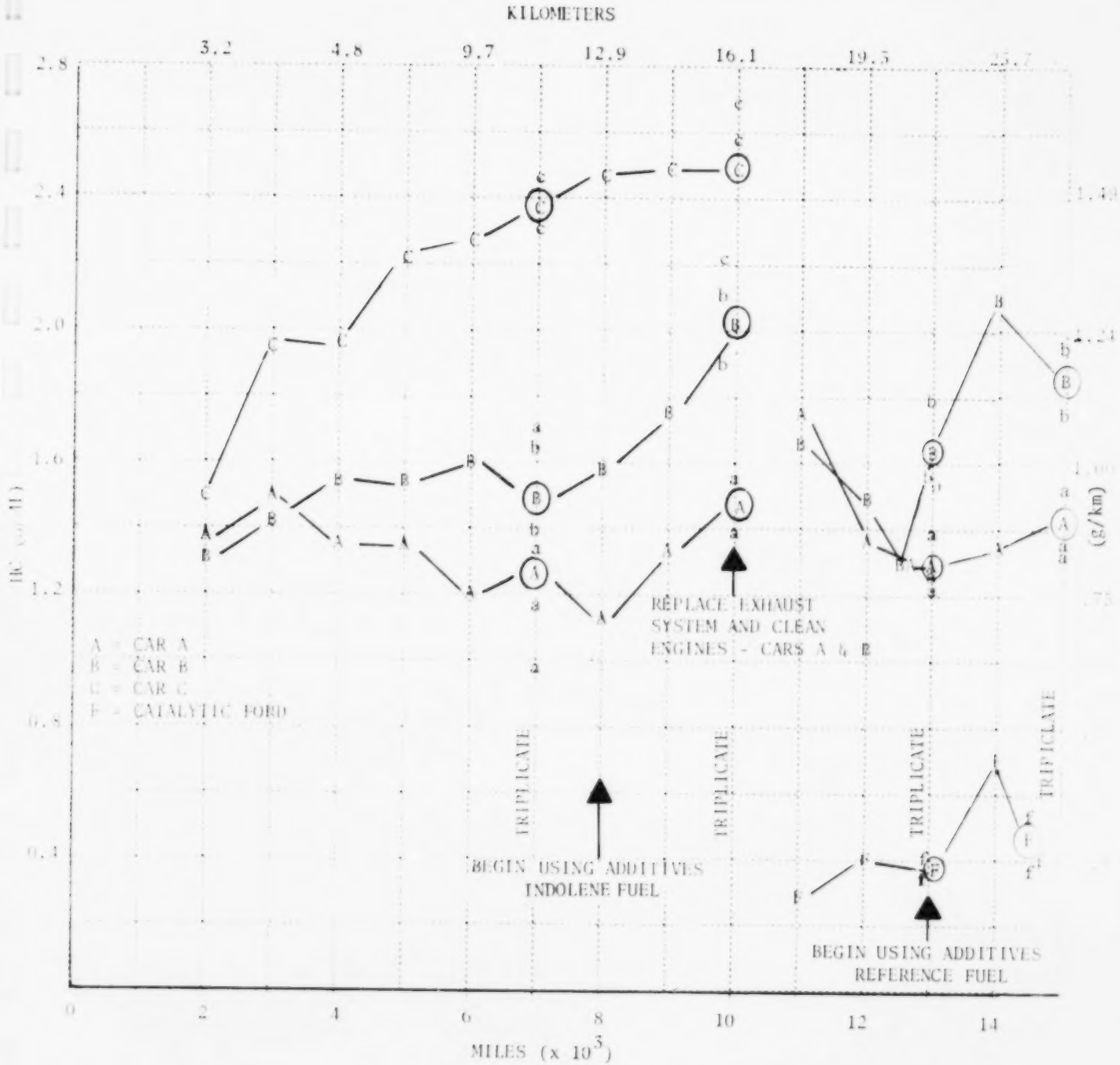


FIGURE 18. HYDROCARBON EMISSIONS VS KILOMETERS (MILES) ACCUMULATED ON VEHICLES

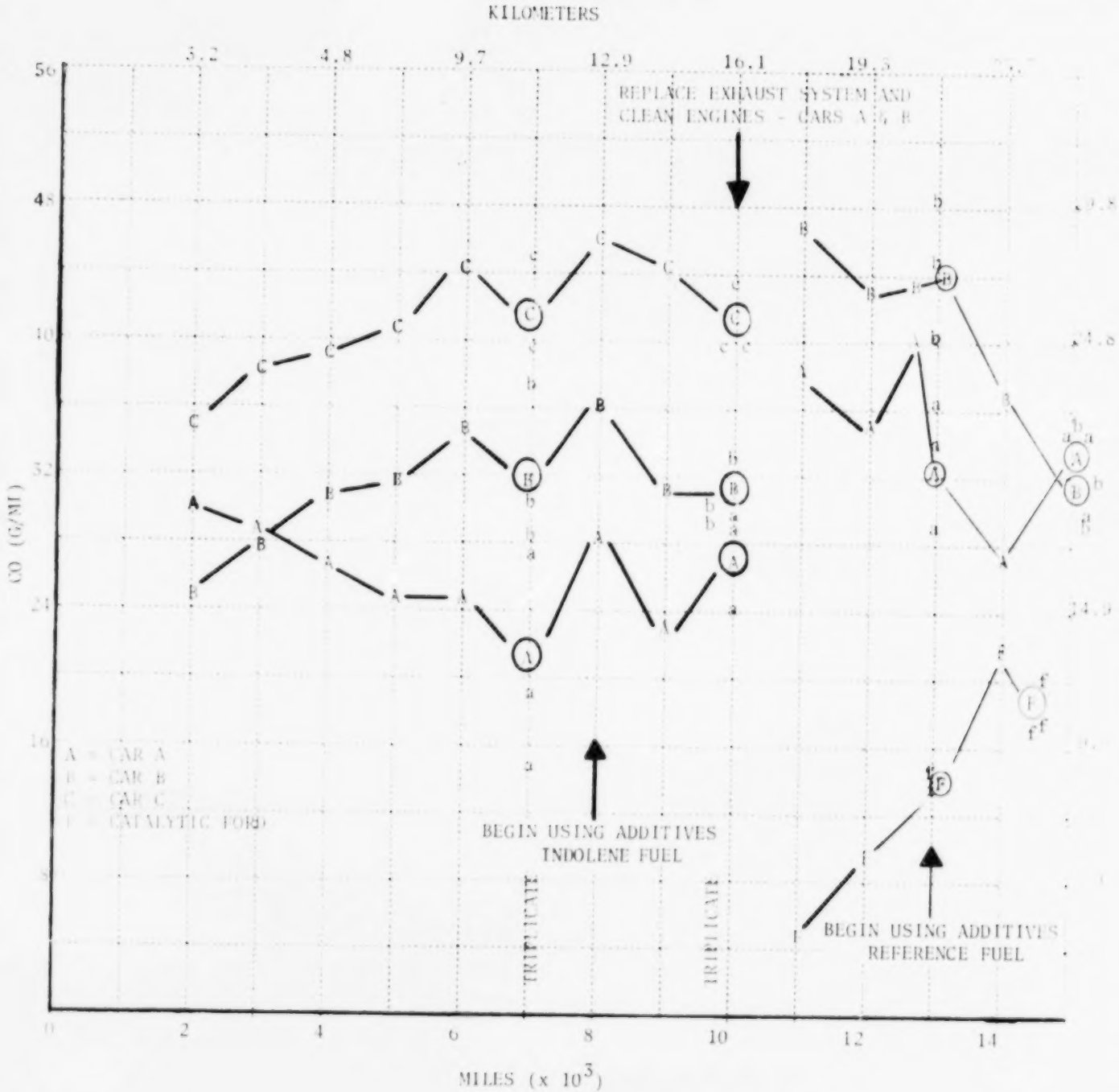


FIGURE 19. CARBON MONOXIDE EMISSIONS VS KILOMETERS (MILES) ACCUMULATED ON VEHICLES

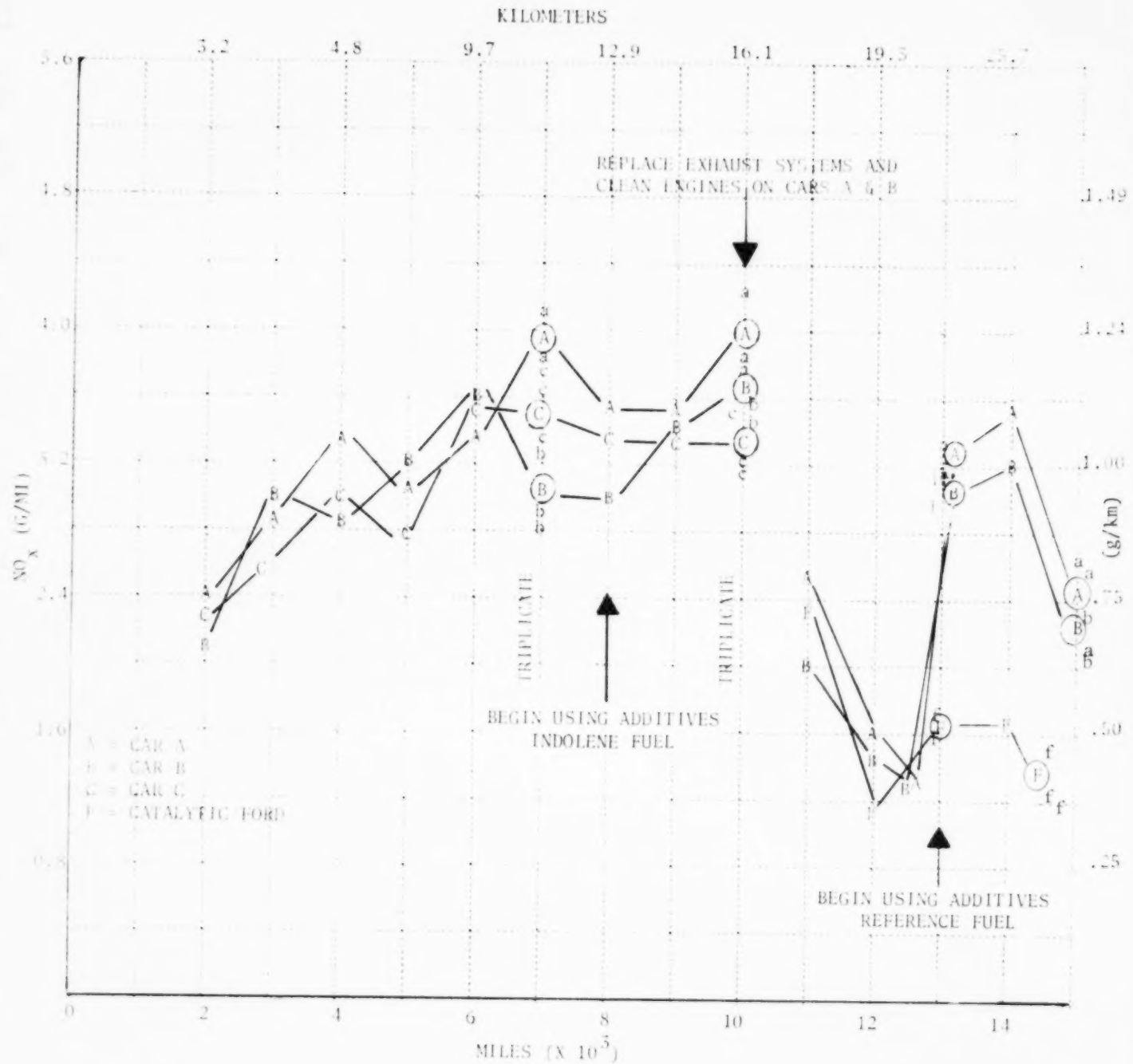


FIGURE 20. OXIDES OF NITROGEN EMISSIONS VS KILOMETERS (MILES ACCUMULATED ON VEHICLES)

catalyst-equipped Ford is predictably much lower in HC emissions, generally averaging about 0.9 g/km (0.5 g/mile). Repeatability of test results at the 20,920 and 24,140 km (13,000 and 15,000 mile) points are improved over earlier triplicate emissions tests, probably because of the controlled humidity air supply system.

The CO emissions for Cars A and B averaged about 20 g/km (32 g/mile) and showed a downward trend during the last 8,045 km (see Figure 19). The final average values are comparable to those observed during the Phase I portion of the program. The catalyst Ford showed a marked increase in CO emissions throughtout most of the distance accumulation period. When the Ford was first received, its CO level was 2.6 g/km (4.2 g/mile), in good agreement with previous EPA measurements of 2.7 g/km (4.34 g/mile). Since that time, the CO level increased to a high of almost 13 g/km (21 g/mile) at the 22,530 km (14,000 mile) point. Decreased catalyst efficiency or a richer air/fuel ratio are possible causes; however, these conjectures are not consistent with the relatively stable HC data for this vehicle over the same period. It is worth noting that substantial deposits were found in the carburetor of the Ford at the 19,310 km (12,000 mile) point, causing it to run excessively rich; at that point, the carburetor was cleaned and rebuilt, and the idle air/fuel ratio reset to specifications. Because of the steady increase in CO emissions, operation of the catalyst-equipped Ford was terminated shortly after reaching the 22,530 km (14,000 mile) point. As shown, excellent repeatability of CO test results was observed in both sets of triplicate tests on the Ford.

The NO_x emissions showed the greatest variability as a function of distance accumulation for all three cars (see Figure 20). The catalyst Ford had lower NO_x emissions than Cars A and B, which showed sharp increases in NO_x emissions between 19,310 and 22,530 km (12,000 and 14,000 miles). Complete system leak checks and analytical calibration showed no abnormalities. The fact that the NO_x levels of Cars A and B 4,830km (3,000 miles) after engine cleaning were consistent with those obtained after the initial 4,830 km (3,000 miles) accumulation suggests that the cars were behaving normally throughout the testing period. Reproducibility of NO_x test results in both triplicate emissions series was excellent for all cars.

3.2.2 Phase II Repeatability Tests - EPA Reference Fuel

Triplicate repeatability tests using the recommended methodology were performed in the Calspan smog chamber at the 20,920 and 24,140 km (13,000 and 15,000 mile) accumulation points. As before, the tests involved driving the first 23 minutes of the LA-4 driving cycle on a chassis dynamometer, while a fixed portion (300:1 dilution ratio) of the auto exhaust was admitted into the smog chamber. After adding 0.05 ppm SO_2 to the chamber air and regulating the temperature to 26.5°C (80°F), the sample was irradiated for 23 hours while the reactants and visibility were continuously monitored.

All three cars were operated on the identical, additive-free EPA reference fuel (sulfur content 124 ppm) until reaching the 20,920 km (13,000 mile) point. After performing triplicate emissions and visibility tests, the additives F-310 and CI-2 were introduced into the fuels of Cars A and B and thiophene to the fuel of the catalyst Ford (sulfur content approximately 1,000 ppm). A similar set of tests were conducted at the 24,140 km (15,000 mile) point. Results of the visibility analysis are summarized in Table III.

The data in Table III show that the final visibilities for Cars A and B at the 20,920 km (13,000 mile) point are dramatically improved over earlier test results. Although nearly identical test procedures were used, the final visibilities using the non-leaded, low sulfur reference fuel, were found to be much better than in tests using commercial grade non-leaded and low-lead indolene fuel. The low sulfur content of the reference fuel is the main difference in the fuels and is thought to be responsible for the observed differences in results. As before, the greatest scatter in the data was observed for Car A. The catalyst-equipped Ford was the cleanest of the test vehicles at this point, both in terms of HC and NO_x emissions and final visibility after irradiation.

After introducing additives into the fuels of Cars A and B and thiophene into the fuel of the Ford, triplicate emissions tests were again performed at 24,140 km (15,000 miles). Here, the greatest difference in test results can be found in the data for the catalyst Ford. The addition of sulfur

TABLE III.

RESULTS OF VISIBILITY ANALYSIS FROM METHODOLOGY REPEATABILITY TESTS

CARS A, B, C, AND CATALYTIC CONVERTER EQUIPPED FORD

Test Condition	VISIBILITY IN KILOMETERS (MILES) AFTER 23 HOURS IRRADIATION				
	12,900 km (8,000 mi.)	16,100 km (10,000 mi.)	START USING EPA REFERENCE FUEL	20,920km (13,000 mi.)	24,140 km (15,000 mi.)
CAR A 300:1 + 0.05 SO_2 non-leaded fuel + F-310	17.2, 29.8, 33.0 — 30.9±2.1 (19.2±1.3)	35.1, 61.1, 46.7, 27.3 — 42.5±19 (26.4±12)		77, 106, 88, 72 — 87±16 (54±10)	93, 92, 116 — 100±16 (62±10) Reference fuel plus F310
CAR B 300:1 + 0.05 SO_2 non-leaded fuel + CI-2	36.6, 36.7, 33.0 — 33.5±3.2 (20.8±2.0)	35.1, 36.8, 27.0, 9.6 — 31.9±5.0 (19.8±3.1)		63, 66, 76, 64 — 68±8 (42±5)	42, 51, 45 — 47±5 (29±3) Reference fuel plus CI-2
CAR C 300:1 + 0.05 SO_2 low lead fuel + + CI-2	28.2, 29.0, 22.5 — 26.5±4.0 (16.5±2.5)	15.1, 12.4, 15.8 — 14.3±1.9 (8.9±1.2)		--	--
FORD EPA Reference Fuel	--	--		85, 95, 98 — 93±8 (58±5)	47, 42, 37 — 42±5 (26±3) Reference fuel plus thiophene

to the fuel also resulted in substantial lowering of visibility after irradiation. For example, the average visibility after irradiation for the Ford without sulfur was 93±8 km (58±5 miles), whereas with the added thiophene, the average measured final visibility was 42±5 km (26±3 miles). Visibility data showing these differences can be seen in Figure 21.* The actual concentrations of sulfur-containing compounds observed in the smog chamber were ~0.01 ppm for tests performed at 20,920 km (13,000 miles) and 0.15 ppm (expected to be mainly in the form of H_2SO_4 mist) for the tests at 24,140 km (15,000 miles). This large difference can easily account for the observed lowering in final visibility.

Another important difference in test results can be found in the data for Car E. After introducing the additive CI-2 into the fuel at 13,000 miles, lower visibilities were observed. The additive CI-2 is an organomanganese compound (Methylcyclopentadienylmanganese Tricarbonyl). This additive is known to be converted almost completely to a manganese oxide form, mainly Mn_3O_4, in the automobile exhaust. Even the small fraction of unburned CI-2 in the exhaust is likewise decomposed rapidly to manganese oxides and carbonates in the atmosphere by photolytic processes. Manganese species in the form of fine particulate aerosols, as generated from automotive exhaust emissions, are known to be effective in catalyzing the oxidation of SO_2 to sulfate (Matteson et al., 1969). It appears that in the case of low sulfur EPA reference fuel, the enhanced SO_2 photooxidation due to manganese aerosol catalysis may be responsible for the observed lower visibility. In the earlier series of tests with the higher sulfur content fuel at the 16,100 km (10,000 mile) point, an effect of CI-2 was to cause a marked influence on the initial visibility in the smog chamber. Other contributions may have been masked by appreciable SO_2 to sulfate conversion even in the absence of a catalyst.

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*For this particular example, the full range of visibilities is shown. In all previous examples, the common practice of designating 80+ km (50+ miles) as unrestricted visibility has been followed.

M.J. Matteson, W. Stoober, and H. Luther, Ind. Eng. Chem. Fundamentals, 8, 677 (1969).

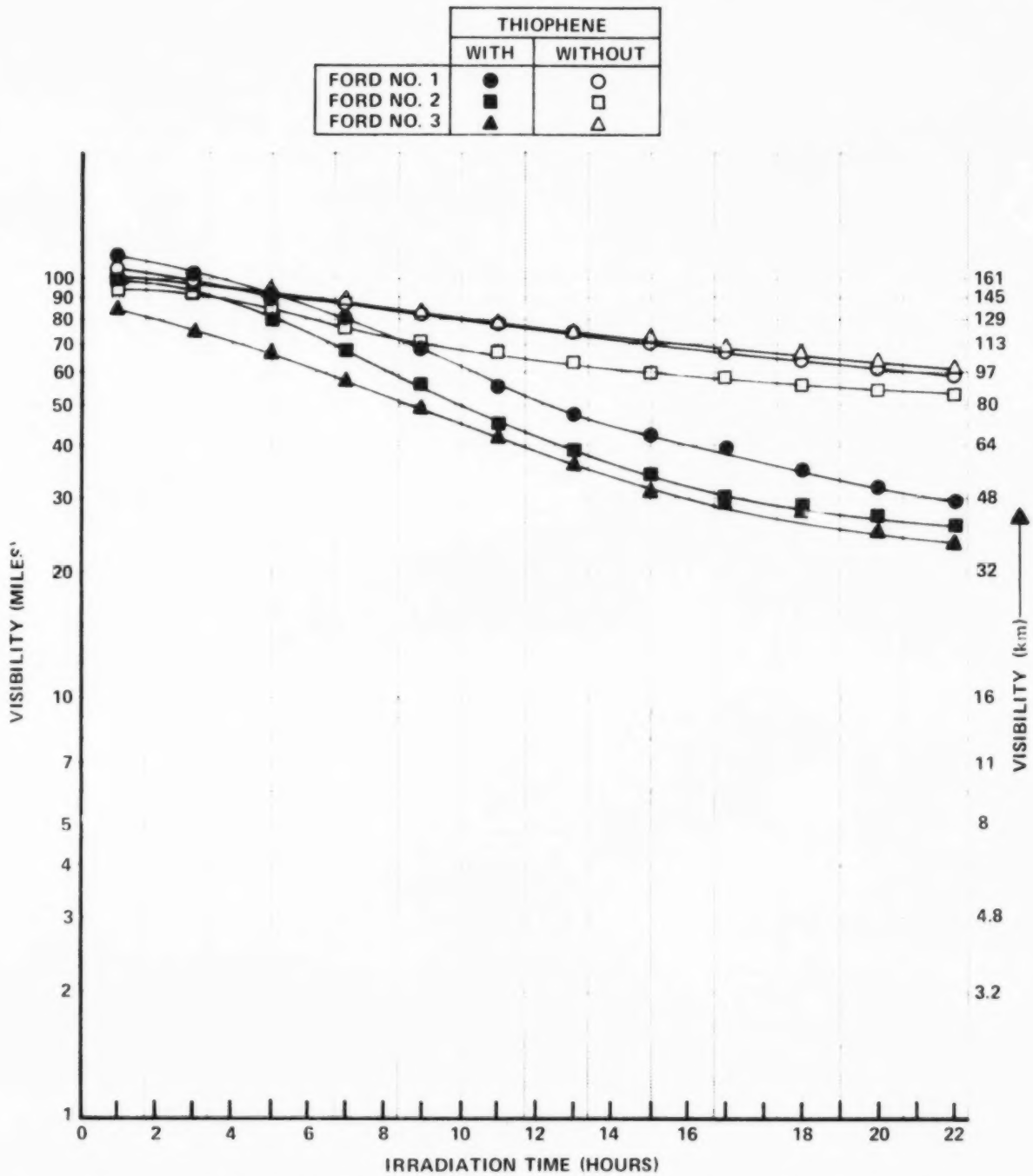

Figure 21 VISIBILITY DATA FOR CATALYST EQUIPPED FORD WITH AND WITHOUT THE ADDITION OF THIOPHENE

Further insight into the relevance of these differences with respect to earlier tests can be found from the data in Figure 22 showing final visibility after 23 hours irradiation vs. initial HC/NO ratio for all tests. The most recent data generated using the reference fuel show a similar correlation of visibility with initial HC/NO ratio, but the data points lie along a different straight line. Although only two types of fuel were tested on this program, it seems possible that a family of curves could be established for representative fuel types, those with high sulfur content lying lower on the scale than low sulfur-bearing fuels. Thus, all three cars using the low sulfur reference fuel were found to lie along the uppermost line. Although only three tests were performed with the catalyst Ford using the sulfurated fuel, the data show that the addition of thiophene to the fuel produced more reactive emissions and visibilities which were substantially lower than in the absence of the thiophene additive. The introduction of H_2SO_4 droplets and the photooxidation of SO_2 to form acid particles can be expected to produce substantial light scattering aerosol when photo-irradiated. The conclusion to be drawn is that high sulfur-bearing fuels, when used even in catalyst-equipped cars, can produce lower visibilities than non-catalyst cars being operated on sulfur-free fuel.

A final point worth mentioning is that the addition of the additive CI-2 to the reference fuel of Car B produced substantially lower visibilities than without the additive. The suspected reasons for the catalytic effect of the additive on the final observed visibility have already been discussed. The data in Table III and those plotted in Figure 22 show that the points do not lie along either of the straight lines for the fuels used in that vehicle. There is insufficient data to state that the effect of the additive is conclusive; however, based on the repeatability of the triplicate emissions and methodology tests, there appears to be an effect which can be measured. As in any experimental program involving a large number of variables, a greater number of tests is needed to statistically validate these initial findings. The recommended methodology appears capable of identifying the effects of individual test variables. Large numbers of tests encompassing a sufficient matrix of test variables would have to be performed if the nature and extent of the visibility effect of an individual fuel or additive is to be ascertained.

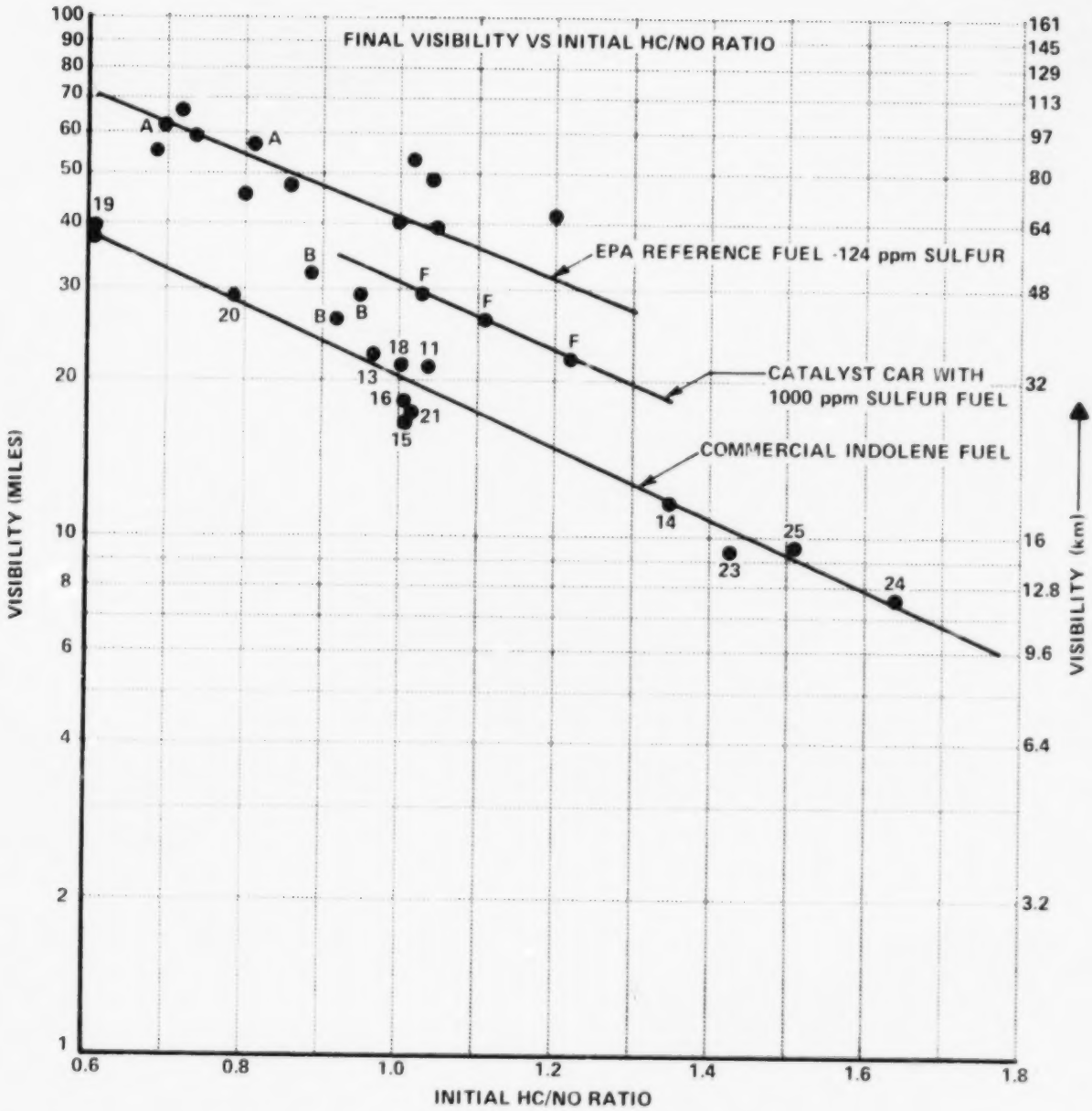

Figure 22 FINAL VISIBILITY IN SMOG CHAMBER VS INITIAL HC/NO RATIO – LETTERS DESIGNATE DATA (CARS A, B, AND F) FROM FINAL TEST SERIES USING ADDITIVES IN EPA REFERENCE FUEL

Section 4

SUMMARY AND CONCLUSIONS

It has been the objective of this program to develop a methodology for determining the effect of fuel and fuel additive combustion products on atmospheric visibility. Three 1972 5.73 liter (350 CID) Chevrolets and one 1973 catalyst-equipped 6.55 liter (400 CID) Ford Galaxie were used in the study. As part of the methodology development, a wide range of experimental conditions were tested in Calspan's 590 m^3 (20,800 ft^3) smog chamber. The effects on test results of exhaust dilution ratio, relative humidity, added SO_2, primary particulates, evaporative emissions, and irradiation time were investigated. From these investigations, a methodology was developed which involves measuring visibility in a large smog chamber after first introducing auto exhaust at a 300:1 dilution ratio, adding 0.05 ppm SO_2 and irradiating the sample for 23 hours. In each case, vehicles were operated in an identical manner on a chassis dynamometer while a fixed portion of the exhaust was diverted to the chamber. From the triplicate emissions and smog chamber tests, the following conclusions can be drawn:

(1) Using commercial grade indolene fuel, the effects on visibility of the additives F-310 and CI-2 are small compared to the effects brought about by natural variations in engine performance.

(2) The combined effect of Ethyl CI-2 with low-lead indolene fuel had a marked influence on the initial visibility lowering in the smog chamber. No other combination of fuels or additives showed this effect.

(3) The additive CI-2 in combination with the lead-free, low sulfur reference fuel produced substantially lower visiblities than without the additive. Catalytic effects of the additive on the photooxidation of SO_2 are suspected.

(4) The tests show that primary particulates play an important role in the initial and final visibilities noted in the smog chamber. Irradiations of HC + NO + SO_2 mixtures comparable to those found in auto exhaust do not produce equivalent visibility losses.

(5) The final visibility achieved after irradiation of a 300:1 exhaust plus filtered air mixture with 0.05 ppm added SO_2 is closely correlated with the initial HC/NO ratio in the chamber. The correlation for the commercial grade indolene is so good that final visibilities can be predicted from an initial measurement of total HC and nitric oxide in the chamber. Data generated using EPA reference fuel show a similar correlation of visibility with HC/NO ratio, but the data lie on a different straight line. Although only two fuel types were investigated in this study, the correlation seems to be sufficiently high so that a family of lines could be established for representative fuel types, those fuels with high sulfur content lying lowest on the visibility scale.

(6) The catalyst-equipped vehicle operated on reference fuel (124 ppm) sulfur) produced the least emissions but not necessarily the best visibility in the smog chamber; i.e., the initial HC/NO ratio was still the most important factor in determining the final visibility after irradiation. There are limits to which this relationship can be carried, obviously, since reductions in both the total HC and oxides of nitrogen in the natural atmosphere would favor less severe smog.

(7) Operation of the catalyst car on high sulfur content (~1,000 ppm) reference fuel had a large effect on lowering the final visibilities observed in the smog chamber. In fact, for the fuels and additives tested at a given HC/NO ratio, the sulfur content of the fuel appeared to have the most important effect on final visibility.

(8) In addition to having the expected initial effect on lowering visibility, primary particulates in auto exhaust were found to play an important role in long-term visibility reduction (i.e., after 23 hours irradiation).

From the tests performed on this program, it appears that a sufficiently sensitive methodology has been developed to assess the effects of fuels and additives on atmospheric visibility. While the tests were performed exclusively in a smog chamber, it is believed that the uniquely large facility provides sufficient realism to allow assessment of fuel and additive effects.

The methodology appears well suited to testing the effect of variations in catalyst-type, sulfur content of fuels, fuel composition and engine modifications. A baseline of data points has been established for comparison with future experiments. Additional tests are needed to identify the most important factors which influence total aerosol formation. With a sufficient data base, it may be possible to develop a simple tailpipe measurement which could be used to predict the effects of different fuel types on atmospheric visibility.

It is recommended that additional experimentation with fuels, engines and emission controls be run to allow full understanding of the potential effects of proposed improvements in auto emission control technology.